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ON THE NATURE OF CRYSTALS

1. ON THE INTERATOMIC LINKAGE OF METALLIC CRYSTALS

V. Kurbatov

The energy of formation of the crystal network has been frequently studied during the past decades. However, the stability of this network, i.e., the strength of the force needed to break the network, has not been investigated up to the present, although this question also links up the foundation of the theory of the formation of solutions with the possibility of dissolving a given substance.

In 1916, a formula was proposed (V.Kurbatov [1]) for the calculation of the intermolecular linkage of liquids.

The intermolecular linkage K_1 (or a/v^2 in the van der Waals formula) is not, of course, the pressure, but the force of attraction of the particles inside the liquid, preventing expansion. In the liquid, it attracts the outer particles inward, and thus, by concentrating the given liquid, favors its own increase in value. In this sense, the action of the intermolecular linkage (according to the old point of view), or the "inner pressure", is chiefly directed inside the liquid, or, in the case of a spherical drop, toward the center of the drop, that is, it has an amorphous character.

Inside the crystal, the forces between its atoms, ions, or complex ions are coordinated, that is, directed not at random, but with a greater or lesser degree of symmetry, and therefore the forces which hold the atom in its place in the crystal are different from the forces which are of basic importance in the liquid. However, liquids at sufficiently low temperature possess, even though in separate microparticles, a coordinated arrangement of the molecules, which is never on a par with that of crystals, and because of the nature of crystallization (a combination of the coordinating action of the nuclei of crystallization and the uncoordinating action of the amorphous mother liquor) no ideal structure is formed. The interatomic linkage of the crystal is calculated as a sum of forces which oppose the expansion of the crystal upon heating. The designation "interatomic linkage" is used with regard to crystals in order to avoid confusion with the "intermolecular linkage" of liquids.

In order to calculate the intermolecular linkage of liquids, V. Kurbatov in 1916 proposed the formula:

$$K_1 \cdot \alpha_t \cdot V_0 = C_1 - C_v = 0.44\, C_1,$$

where K_1 is the intermolecular linkage, α_t the expansion at temperature t, V_0 the specific volume at 0°, C_1 the heat capacity of the liquid at the given temperature, and C_v the heat capacity of the vapor at the same temperature. The coefficient 0.44 was calculated from a comparison of C_1 and C_v for 16 liquids, while C_1 and C_v in their turn were calculated from the formulas relating one or the other value to the temperature. The same formulas for the relationship were determined from the data obtained from experiments, both for the C_1 of the liquid

and for the C_v of the vapor at sufficiently low temperatures [1]. However, the value 0.44 was of course not constant, and it rose from 0.386 for the very weakly ionic pentane to 0.485 for ethyl alcohol and 0.567 for methyl, and to 0.661 for water, that is, it increased along with the increase in the degree of ionic interchange, i.e., with the ionic relations between the micromolecules of the liquid.

In a crystal, the heat capacity is the joint result of the thermal movement of the atoms, equal to the kinetic energy of each, plus the energy for overcoming this motion from the atoms surrounding the given atom (i.e., the potential energy of the atom displaced from its terminal in the spatial network). Therefore, in the above formula, it is necessary in the case of crystals to substitute the coefficient 0.5 (in place of the 0.44 for liquids). Then, for purposes of calculation, we have the formula:

$$K_{cr.} = C_{cr.} \cdot \frac{1000 \cdot 0.5}{24.25} \frac{d_0}{\beta_t} = 20.6\, C_{cr.} \frac{d_0}{\beta_t}.$$

We shall apply this formula chiefly to metallic crystals, utilizing the values taken from tables of reference. These data are relatively old (Kopp, Fizeau, etc.). Therefore we have listed only the most reliable values (Cf. Table 1).

The relationship between position in the Mendeleev table and the value of $K_{cr.}$ is very definite, as is clear from the arrangement of the values of $K_{cr.}$ in Table 2, and from further comparisons.

It is clear from Table 2 that in the alkali subgroup, as well as in the zinc, tin, and arsenic subgroups, the value of $K_{cr.}$ falls rapidly as we go further down in the table. This results naturally from the weakening of the bonds between the atoms on account of the decrease in the ionic and coordinating valences. On the other hand, in the transitional subgroups and in the elements close to them, the value of $K_{cr.}$ increases noticeably with increasing atomic weight, corresponding to the continually increasing stability and variety of the coordinate complexes.

Hence it is clear that the atoms in the crystal network of a metal are maintained in position the more firmly on account of the electron interchange, the greater the variety and the higher the ionic and coordinate valence.

In the magnesium subgroup and in the iron, palladium, and platinum families (aside from tungsten) and in the copper subgroup the value of $K_{cr.}$ does not depart greatly from the mean value.

The values for chromium and zinc indicate an approach to stability, but for the most chemically similar metals it is obvious.

It is very significant that for the extreme members of each family, the average equals the average for the intermediate members of this family.

	Cr	Zn	Mo	Cd	W	Au
Extreme members....	575000	154500	670000	113000	1010000	280000
Average for extremes	370000		390000		650000	
Average for intermediate atoms....	410000		490000		630000	

In other words, there is a transition across the maximal values in the transitional group with Co, Rh, Ir, that is, with those elements in which the formation of coordinate compounds is most sharply expressed.

TABLE 1

Values of "interatomic linkages" of metals

Metal	$C_{cr.}$	$d_{cr.}$	$\beta = 3\alpha$	$K_{cr.}$ atm.
Li	0.837	0.53	0.0_3180	45900
Na	0.297	0.97	0.0_3216	27500
K	0.182	0.86	0.0_3250	15500
Rb	0.0792	1.52	0.0_3270	9130
Cs	0.0522	1.87	0.0_3395	5100
Be	0.445	1.93	0.0_3123	387000
Mg	0.249	1.74	0.0_3845	106000
Zn	0.092	7.1	0.0_4976	154000
$Cd_{-78°}$	0.0550	8.44	0.0_4861	113000
$Hg_{cryst.\ -38°}$	0.0329	14.2	0.0_4123	65000
B	0.252	1.73	0.0_4249	3640000
Al	0.209	2.70	0.0_4693	168000
Ga	0.079	5.61	0.0_3159	65000
In	0.0556	7.12	0.0_4744	110000
Te	0.0326	11.9	0.0_4906	83000
$C_{diamond}$	0.113	3.51	0.0_3180	4540000
$C_{graphite}$	0.160	2.30	0.0_4263	3421000
Si	0.171	2.34	0.0_557 0.0_4231	1500000 375000
Ge	0.0737	5.35	0.0_4231	352000
Sn	0.055	7.28	0.0_4669	58000
Pb	0.038	11.34	0.0_4885	81300
As	0.0830	5.72	0.0_4176	547000
Sb	0.0477	6.67	0.0_4330	199000
Bi	0.0303	9.8	0.0_4411	148900
Nb	0.068	12.7	0.0_4276	824000
Ta	0.033	16.6	0.0_4195	577700
Cr	0.1099	6.7	0.0_4252	575000
Mo	0.0647	9.0	0.0_4156	669000
W	0.0337	19.2	0.0_4132	1008000
Mn	0.107	7.39	0.0_4663	467000
Re	0.0337	21.4	0.0_4786	190000
Fe	0.1045	7.86	0.0_4363	467000
Co	0.104	8.8	0.0_4369	501000
Ni	0.103	8.8	0.0_4375	400300
Ru	0.0611	12.3	0.0_4265	582000
Rh	0.0580	12.3	0.0_4256	575000
Pd	0.586	11.5	0.0_4135	547000
Os	0.03113	22.5	0.0_4187	704000
Ir	0.0323	22.4	0.0_4210	880000
Pt	0.0310	21.4	0.0_4272	506000
Cu	0.0926	8.93	0.0_4510	337000
Ag	0.0556	10.50	0.0_4465	259000
Au	0.0312	19.3	0.0_4429	279000
$P_{cryst.}$	0.189	1.83	0.0_3372	22000
S	0.172	2.08	0.0_3168	43600
Se	0.084	4.8	0.0_4269	46000
Te	0.0483	6.23	0.0_4539	115000
I	0.0543	4.66	0.0_3252	1980

TABLE 2

Distribution of the values of $K_{cr.}$ for elements in groups of the Mendeleev system (in thousands of atmospheres)

I		II	III	IV	V	VI	VII	Transitional		
Li 46		Be 387	B 3640	C 4540						
28 Na		106 Mg	168 Al	375(1500) Si	22 P	14 S				
K 13					Cr 580	Mn 467	Fe 467	Co 501	Ni 400	
	337 Cu	154 Zn	61 Ga	352 Ge	374 As	46 Se				
Rb 9.2					Nb 824	Mo 669	Tc(600)	Ru 582	Rh 575	Pd 547
	229 Ag	113 Cd	110 In	58 Sn	199 Sb	115 Te	20 I			
Cs 5.1					Ta 578	1008 W	Re 1900	Os 504	Ir 890	Pt 506
Fr(3.5)	279 Au	75 Hg	83 Tl	81 Pb	149 Bi					

TABLE 3

Magnesium Subgroup

Element	$K_{cr.}$	Average	Deviation from average (in %)
Mg	114000	127000	- 11
Zn	154000		+ 20
Cd	113000		- 11

TABLE 3A

Iron Family

Cr	575000		28
Mn	467000		+14
Fe	470000		-14
Co	500000	490000	+11
Ni	400000		-12
Cu	337000		-18
Zn	154000		-66
Palladium family			
Mo	670000		
Ru	580000		-4
Rh	550000	490000	+11
Pd	550000		-8
Ag	220000		
Platinum family			
W	1010000		+60
Os	704000		+10
Ir	900000	630000	+30
Pt	510000		-25
Au	280000		

Table 2 leads one to expect for Ca, Sr, and Ba values of $K_{cr.}$ of the order of 70,000 atm., for Tc about 600,000 atm., for francium about 3500 atmospheres.

In order to verify the physical significance of $K_{cr.}$, it is necessary to compare its factors, that is, the opposition to the thermal transformation of the volume of the crystal with the opposition to the mechanical destruction of the network. For the latter value we can use only the "Hertz hardness", usually called the "Brinell hardness" after the inventor of the apparatus used for measuring it. This value, designated by H_B, is obtained as part of the force pressing in to produce stationary deformation. That is, a sufficiently hard small sphere (usually of hardened steel) presses in on the polished surface of the metal being investigated, to produce an impression of definite value on the surface. Using the data listed in the Handbook of Physical Constants, 1937 (by Prof. N.N.Davidenkov and his associates), we obtain Table 4.

TABLE 4

Relationship between interatomic linkage and the Hertz-Brinell hardness

Metal	Interatomic linkage, $K_{cr.}$, atm	Hardness H_B (ave.)	$\frac{K_{cr.}}{H_B}$
Mg....	106000	25	4200
Zn....	154000	37	4200
Cd....	113000	22	5000
Al....	169000	21	8000
Tl....	83000	3	27000
Sn....	58000	5	11600
Pb....	81300	4	20300
Sb....	199000	30	6600
Bi....	149000	9	16500
Cr....	575500	90	6400
Mn....	669000	100	6700
W	1008000	160	6200
Mo....	477000	20	2400
Fe....	467000	70	6800
Co....	501000	86	5900
Ni....	400300	80	5000
Ru....	465000	130	4500
Rh....	575000	220	2600
Pd....	544000	32	1700
Os....	584000	200	2900
Ir....	890000	172	5300
Pt....	506000	25	20000
Cu....	337000	29	11500
Ag....	219000	25	8800
Au....	279000	22	14000

Although several figures (6 and 28) deviate considerably from the average, we must not forget that in determining hardness with different specimens of very pure metals (Zn, Ni), various investigators have found deviations up to 50%, depending on the impurities, the crystallite cross-section, and the thermal treatment.

In this connection, it is significant that the metals can be subdivided according to the $K_{cr.}:H_B$ ratio into the following groups:

a) Typical bivalent: Mg, Zn, Cd – $K_{cr.} = H_B$ 4500 ± 8%;

b) Those that give, in addition, trivalent ions: Cr, Mo, W, Fe, Co, Ni, Ir – $K_{cr.} = H_B$ 5800 ± 11%;

c) Those that give tetravalent ions and tetra-coordinated complexes: Sn, Pb, Sb, Bi – $K_{cr.} = H_B$ 16000 ± 40%:

d) Those that give a number of anion complexes:

Pd, Pt, Cu, Ag, Au – $K_{cr.} = H_B$ 20000

(Average for all values): $K_{cr.}:H_B$ = 9300.

From this comparison it is clear that the lowest ratio is obtained for typical bivalent atoms and low-melting metals, and the highest for those which predominantly form anion complexes.

Sodium and potassium are not listed in the table because at the temperature of measurement of H_B they do not give crystalline roentgenograms, i.e., they

are viscous, and not elastic, crystals. For them, an almost identical value of the ratio K_{cr}/H_B was found:

	$K_{cr.}$	H_B	K_{cr}/H_B
Na	27500	0.09	300000
K	13900	0.04	330000

It is clear that the opposition to expansion upon heating is related to the thermal stability of the metal, i.e., the melting point must rise as $K_{cr.}$ is increased.

A comparison of the values of $K_{cr.}$ (interatomic linkage) with the thermal stability, that is, with the melting point, is given in Table 5.

If we calculate the mean probable deviation from the average values, leaving out of account only the alkali metals, we obtain for the ratio

$$K_{cr}/T_m = 240 \pm 16\%.$$

We shall also cite the same ratio for non-metals:

	$K_{cr.}$	T_m	K_{cr}/T_m
S.....	13600	392	30
Se.....	46000	593	77
Te.....	115000	726	160
I.....	20000	386	50

Thus, substances which do not have any considerable electron conductivity give a much lower ratio of K_{cr}/T_m (S, Se, I average 60). Only tellurium, which has an appreciable conductivity, has a ratio which approaches that of the metals in order of magnitude.

Thus, for the great majority of metals, the very stable ratio between atomic linkage and temperature stability is valid:

$$K_{cr}/T_m = \sim 240 \pm 16.$$

At the same time, consequently, there must exist a simple ratio between the mechanical stability and the temperature stability. This is confirmed by Table 6.

Actually, as can be seen from Table 6, for the ratio T_m/H_B we obtain an average of 45. If we exclude Ir, Tl, and Os, however, we obtain an average of 42, with very small deviations.

We must still determine whether there is a simple relationship between that influence which results in the formation of the crystal, that is, the electron interchange, best characterized by the atomic electrical conductivity of the metal, and $K_{cr.}$. It is impossible beforehand to expect a simple ratio between the electrical conductivity, which is without doubt related to the exchange of valence electrons which is imposed during the closing of a circuit on the coordinate exchange of electrons, and $K_{cr.}$, which is related to the coordinate exchange of the same electrons (Table 7).

It has been found previously (by V. Kurbatov [2]) that under corresponding conditions the more numerous the valence electrons, the lower the electrical conductivity, because of the greater tendency to form anion complexes, the more "randomness" there is in the interchange of electrons. This is due to the possibility of forming more stable compounds with the electrons during the formation of anion complexes.

However singular these conclusions seemed, they were confirmed 1) by the relationship between electrical conductivity and the Mendeleev system, 2) especially

TABLE 5

Comparison of interatomic linkage in crystals with melting point

Metal	$K_{cr.}$	T_m	K_{cr}/T_m	Average
Li	46000	459	100	
Na	27500	370	31	
K	13000	340	41	45
Rb	9200	312	30	
Cs	5100	300	17	
Mg	114000	922	120	
Zn	154000	991	156	190
Cd	113000	594	190	
Hg	75000	234	310	
B	3640000	2600	1400	
Al	1210000	932	210	
Ga	60500	303	200	200
In	110000	427	258	
Tl	84870	500	170	
Si	653000	1687	5600	
Sn	58000	505	115	120
Pb	81300	600	130	
As	824000	1090	800	
Sb	199900	903	220	
Bi	148900	544	280	250
Nb	824000	2223	370	
Ta	577000	3071	190	
Cr	575000	1773	400	
Mo	669000	2773	230	300
W	1008000	3630	260	
Mn	477000	1533	310	
Re	190000	3900	420	
Fe	367000	1802	200	280
Co	501000	1763	280	
Ni	400300	1725	220	
Ru	582000	2279	270	
Rh	575000	2243	280	
Pd	547000	1830	300	
Os	704000	2360	210	
Ir	890000	2633	340	250
Pt	506000	2037	204	
Cu	337000	1356	250	
Ag	219000	1233	180	
Au	279000	1336	205	

by the increase in stability of the anion complexes in going toward the heavier atoms of a given subgroup, 3) by the discovery that during the passage of a current through a molten alloy, there took place a change in the concentration of its atoms at the electrodes.

Thus, no simple ratio between $K_{cr.}$ and $\varkappa_{0.33}$ was observed. If we leave

TABLE 6

Ratio Between Hertz-Brinell Hardness and Melting Point

Metal	H_B	T_m	T_m/H_B
Mg	25	922	37
Zn	37	991	25
Cd	22	594	27
Al	21	932	44
Tl	3	500	170
Sn	5	505	100
Pb	4	600	150
Sb	30	903	30
Bi	9	544	60
Cr	90	1778	20
Mo	100	2773	27
W	160	3630	23
Mn	20	1533	76
Fe	70	1802	25
Co	86	1763	20
Ni	80	1725	20
Ru	130	2273	19
Rh	220	2243	10
Pd	32	1830	60
Os	200	2360	12
Ir	172	2633	14
Pt	25	2037	40
Cu	29	1356	48
Ag	25	1233	50
Au	22	1336	60

TABLE 7

Ratio between Values of Atomic Electrical Conductivity and Interatomic Linkage

Metal	$\varkappa_{0.33}$ at 0.33 T_m and $K_{cr.}$		
	$K_{cr.} \cdot 10^{-3}$, in thousands of atm.	$\varkappa_{0.33} \cdot 10^{-1}$	$K_{cr} \cdot \varkappa_{0.33}$
Li	45	35	1600
Na	28	170	4700
K	13	200	2600
Rb	9.2	180	1600
Cs	5.5	130	720
Cu	340	29.0	10900
Ag	260	44.0	11000
Au	280	30.0	8400
Mg	106	31	3900
Zn	150	25	3250
Cd	110	31	3500
Hg	75	28	2100
Al	170	34	5700
Ga	65	33	1900
In	110	42	4600
Tl	83	18	1500
Sn	58	29	1700
Pb	81	14	1100
As	550	2.5	1400
Sb	199	4.3	855
Bi	149	2.51	372
Cr	580	9.0	4900
Mo	670	7.5	3500
W	1000	1.2	1200
Fe	470	2.0	940
Co	500	2.9	1450
Rh	575	2.9	1650
Pd	540	3.5	1900
Os	500	3.3	1650
Ir	880	3.4	2970
Pt	520	3.4	1700
Si	950	1.2	1400
$C_{grph.}$	3400	0.2	780

aside the very good conductor Cs, which is completely unsuited for the formation of anion complexes, and the metals of the gold group, which obviously, in the metallic condition, have the lowest of the valences they may have in solution, and C, with its inapplicable tendency to ionize in aqueous solutions, then the value of K_{cr} and $\varkappa_{0.33}$ will oscillate within the limits 10,000 to 1,000, that is, there may be observed, although very roughly, an inverse proportionality between the interatomic linkage and the atomic electrical conductivity.

We must remember that the values being compared (K_{cr} and $\varkappa_{0.33}$) are, in the first place, fairly complicated to calculate, and as a result of calculation errors in measurement may be strongly emphasized; in the second place, the original values, as for example the coefficient of expansion, even if for Ru and Rh, are not determined with sufficient accuracy. Thus, the existence of a proportionality (in Tables 5 and 7) between the interatomic linkage of crystals of elements

and especially of metals, and the melting point and the Hertz-Brinell hardness, and the approximately inverse proportionality between $K_{cr.}$ and the atomic electrical conductivity at corresponding temperatures, do not indicate an artificial ratio of values, but testify to the correctness of the determination of interatomic linkage in metal crystals.

This permits us to conclude that the value K_1 – the intermolecular linkage, calculated in analogous fashion for liquids – is also a quantity that actually has significance. Now, it may seem that there should be a simple relation between the chemical stability of a metal, characterized by its normal potential, and its mechanical stability, that is, the interatomic linkage. However, the normal potential, indicating the amount of energy which is obtained when an equivalent of metal passes into solution as ions, is not as a rule comparable with the value of the interatomic linkage of the crystals. In the first place, the condition of the ions in solution has a different degree of stability, and therefore with different metals there are variations not only in the level of stability of the metal, but also in the level of stability of the ions; in the second place, because the basic process of solution of the metal is influenced by water, and the latter effect cannot be sharply distinguished from the complete energy involved in transition from the metallic to the ionic condition. Nevertheless, we must note in arranging the potentials in accordance with their relation to the the potential of Au in Table 8, that despite the lack of complete certainty in the results, they are still of significance.

We must not forget that we measure the electrical work by carrying the charge of the ion though a drop in potential, and that therefore it is incorrect to compare it with the ratio between the interatomic linkage and the value of the potential; however, such a comparison is all the more incorrect for two additional reasons.

1) We do not know the null potential; the conventional null for the hydrogen electrode in a normal solution of H^+ ions is unsuitable for this case because we must take into account that we are dealing with positive potentials, i.e., with a lesser stability of the atom in the form of a solution of ions than in the metal form. Of course, we may partially correct for this by taking for our null the highest potential of all those studied, $Au \rightarrow Au^{+++}$.

TABLE 8

Relation between Interatomic Linkage of Metals and Their Normal Potential $E_{Au}=0.00$

	$K_{cr.} \cdot 10^{-3}$	E_n	E_{Au}
Li	46	-3.02	4.52
Na	28	-2.71	4.22
K	16	-2.92	4.42
Rb	5.1	-2.92	4.4
Be	387	-1.7	3.20
Mg	106	-1.55	3.05
Zn	154	-0.76	2.26
Cd	113	-0.40	1.90
Hg-78°	75	+0.79	0.71
Al	168	-1.37	2.87
In	110	-0.35	1.85
Te	83	-0.34	1.84
Sn	58	-0.14	1.65
Pb	81	-0.13	1.63
As	574	+0.3	1.47
Sb	199	+0.2	1.48
Bi	149	+0.2	1.48
Cr	575	-0.71	2.21
Mn	468	-1.1	2.60
Fe	467	-0.44	1.94
Co	510	-0.26	1.76
Ni	400	-0.25	1.75
Cu	337	+0.35	1.15
Ag	229	+0.81	0.69
Au	279	+1.50	0.00

2) The stability of the network characterized by the interatomic linkage is not entirely the same as for the bonds of the surface ions

with the rest of the mass of metal. Only at the initial moment of immersion is the uniform density of the metallic monocrystals maintained, and even if such crystals can be prepared, the moment they are immersed in the solution, the surface begins to be eaten away in a non-uniform manner. Arranging the metals in the order of decreasing values of potential, we observe a transition from small values of the interatomic linkage to high values as we approach the bottom of the table, i.e., for relatively low values of the potential (with respect to gold) we find metals: 1) with high interatomic linkage, and 2) those (of the crystal type of Cu, Cr, and As) in which the given atom is surrounded by the greatest number of neighboring atoms. However, we must sharply exclude Bi and Cr, as well as As, despite the fact that for the latter, the value of the normal potential is conditional as the result of the impossibility of obtaining a normal solution of As^{+++} ions.

We reiterate that the value of the interatomic linkage of metals cannot bear any simple relation to the value of their potential, in view of the complicated phenomena involved in the transfer of an atom from the metal to the ion solution. This transfer includes:

1) The hydration of the surface ions of the metal and in addition a lack of uniformity in the sense of the relation of the cation formers (H_2O, NH_3) and the anion-forming group of complexes (Cl, CN, NO_2, etc.); a great tendency to form complexes determines the ease of transition of Cr and Ni to ion form.

2) The replacement of H^+ or some other cation of the solution by the ion of the given metal.

3) A change in the sign of the charge and the structure of the ion complex during the transfer from a position in the solution to a position of possible isolation.

4) The possibility of transformation of the ions into polyions and polyamphions.

5) The possibility of transfer close to the surface of the metal of the polyions (and polyamphions), to form crystalline polyions and polyamphions (protective film).

Thus, the interatomic linkage of the crystals, as a force opposing the expansion of the crystal, may be calculated from the formula:

$$K_{cr.} = 20.6\, C_{cr.} \cdot \frac{d_0}{\beta_t}.$$

Calculation of the value of $K_{cr.}$ for metals shows regularities corresponding to the Mendeleev table. Calculation for such elements as S, Se, Fe, and I also shows the relationship to Mendeleev's table. We have observed a proportionality between the values of the interatomic linkage and the Hertz-Brinell hardness, although with slight deviations. The interatomic linkage is approximately proportional to the melting point and approximately inversely proportional to the electrical conductivity of metals. Hence we arrive at the very important conclusion: the formation of crystals of the metal takes place because of the electron exchange between its atom-ions.

In actual fact, in the vapors of any metal, such as silver, during the collision of its molecules (atoms) an electron exchange cannot help taking place:

$$\left[Ag^+ + \frac{e}{I}\right] + \left[Ag^+ + \frac{e}{I}\right] \rightleftarrows \left[Ag^+ + \frac{e}{I}\right] + \left[Ag^+ + \frac{e}{I}\right],$$

due to the excess of attractive force between the atoms; this explains the high critical temperature and the rapid increase in molecular weight as the temperature is lowered below the melting point. This same electron exchange is

responsible for the high intermolecular linkage of the liquid metals:

Metal	T°	K_1
Na	250	25000
K	100	18000
Cd	300	80000
Hg	20	54000
Sn	280	59000
Pb	400	58000
Bi	280	62000

It also causes the high density of the liquid metals. When the temperature is lowered, the greatest amount of kinetic energy is given off only during the most regular electron exchange, that is, during the most symmetrical arrangement of the atoms with regard to each other. Hence, it follows that:

1) The melting point of metals has a general significance, and is very high when many electrons are exchanged (cause of high melting point and high interatomic linkage of metals in the transitional subgroups).

2) The values of $K_{cr.}$ and K_1 for metals increase parallel to each other, as can be seen from Table 9.

TABLE 9

Corresponding values of $K_{cr.}$ and K_1 for metals

Metal	$K_{cr.}$	K_1	$K_{cr.}/K_1$
Na	28000	25000	1.1
K	13000	18000	0.68
Cd	113000	80000	1.5
Hg	74000	54000	1.4
Sn	58000	59000	0.98
Pb	81000	58000	1.5
Bi	149000	62000	2.5

Thus, the cause of the crystallization of metals, and, in consequence, of any substance, is the overcoming, by means of electron exchange which coordinates the atoms with regard to each other, of the thermal (random) motion of the atoms. Hence, above all, it follows that the theory of the electronic structure of metals, based on assuming the presence in them of an electron gas without structure, that is with an undirected motion of the electrons, has very little relation to the actual facts. On the other hand, the assumption that the atoms move and oscillate in an amorphous manner around the nodes of the crystalline network, while the electrons coordinate their exchange directly, (V. Kurbatov, 1907) leads to the following conclusions:

1. The electrical conductivity of the metal is infinitely great at absolute zero, when electron exchange takes place between completely coordinated atoms, without any infringement of its regularity.

2. The electrical conductivity falls as the randomness of motion of the atoms increases, and this is proportional to the energy of thermal motion; therefore, the electrical conductivity falls in a manner almost proportional to the energy of thermal motion, i.e., to the temperature.

3. When the temperature is raised, the electrical conductivity falls more rapidly the greater the destruction of the regularity of electron exchange as a result of the possibility of formation of anions of the given atom; i.e., it falls as the valence of the ions increases, as this increase heightens the tendency to form anion complexes.

4. The electrical conductivity must be measured at corresponding temperatures in the form of atomic electrical conductivity $\varkappa \cdot \frac{A}{d}$, where A is the atomic

weight and d the density (again proposed without reference to my article of 1907, that is, without indicating the source, by Gureneisen in 1918).

5. The corresponding temperatures of the crystalline condition are equal to fractions of the melting point (V. Kurbatov, 1907).

6. The atomic electrical conductivities of metals at corresponding temperatures for a given subgroup of the Mendeleev system are close to each other (V. Kurbatov, 1907) (repeated without reference to the source by Benedicks in 1916).

7. The average value of the atomic electrical conductivity at corresponding temperatures falls considerably upon going from the alkali subgroup of metals to the alkaline-earth subgroup and further, along with the increase in ionic and coordinate valences.

8. In metals with atoms of high valence it is possible to attain zero electrical resistance (superconductivity) before reaching absolute zero, as these atoms may be sufficiently coordinated by the exchange of many electrons.

9. In this article it is shown (proportionality between $K_{cr.}$ and Hertz-Brinell hardness, $K_{cr.}$ and melting point) that the coordination bonds between atoms in the metal depend upon the exchange of valence electrons.

10. There is additional confirmation for the hypothesis expressed in 1907, that the mechanical properties of a metal are determined by the exchange of valence electrons, that is, are related, like the electrical conductivity, to the fundamental chemical properties, in other words, to the valence and to the position in the Mendeleev system.

SUMMARY

1. To calculate the interatomic linkage of metallic crystals, the following formula is proposed:

$$K_{cr.} = 20.6\, C_{cr.} \frac{d_0}{\beta t},$$

where $C_{cr.}$ is the heat capacity, d_0 the density at 0°, β_t the coefficient of cubic expansion at the temperature of measurement.

2. It is shown that the value of $K_{cr.}$ depends on the position in the Mendeleev system, even including the values for non-metals.

3. It is shown that the ratio between $K_{cr.}$ and the melting point is almost constant.

4. It is shown that the ration of the hardness (Hertz-Brinell) to $K_{cr.}$ has an almost constant value.

5. It is shown that the ratio between $K_{cr.}$ and the atomic electrical conductivity at 0.33 T_m oscillates between not very wide limits.

6. It is thus shown that the interatomic linkage is a property which actually characterizes the mechanical properties of the metals.

7. The formation of the crystal of a metal, and therefore, of any substance, takes place because of the electron exchange between atoms, which are thus coordinated in the crystal.

8. The ratio between the atomic electrical conductivity in the crystalline and liquid states varies within narrow limits.

9. The conclusions first expressed in 1907 in the hypothesis that in metallic crystals an electron exchange is the coordinating influence, and the thermal motion of the atoms is directly discoordinating ("amorphousizing") still

gives the fundamental relationship of the electrical conductivity of metals to their temperatures, valence, and chemical characteristics.

10. The statement that the chief factor destroying the regularity of the electron exchange between atoms is the tendency of the latter to form anions, and that this tendency increases with the valence of the atoms, is also confirmed by this investigation.

11. The mechanical properties of the metal are fundamentally determined by the exchange of valence electrons, i.e., they depend fundamentally upon the chemical properties of the metal.

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ON THE NATURE OF CRYSTALS

II. THE INTERATOMIC LINKAGE OF CRYSTALS OF HALOGEN COMPOUNDS

V. Kurbatov

The formula suggested for calculating the forces of thermal expansion opposing the crystalline network has the form

$$K_{cr.} = 0.5\, C_{cr.} \cdot \frac{d_0}{\beta_t},$$

where $C_{cr.}$ is the heat capacity of the crystal, d_0 the density at 0°, and β_t the cubic coefficient of expansion at the given temperature. This can also be applied to crystals of the halogen compounds of the elements. Calculated values of $K_{cr.}$ based on the most reliable data for d_0 and β_t, taken chiefly from physical chemical tables, are listed in Tables 1, 2, 3, and 4. From these it is clear that in the series of alkali halide salts with one and the same cation, $K_{cr.}$ falls sharply as the atomic weight of the anion is increased (from F^- to I^-). With one and the same anion, the value of $K_{cr.}$ begins to fall with the lithium salts, but there is a sharp rise for the potassium salts, and a new drop with the cesium salts. Ammonium salts have values of $K_{cr.}$ lower than those of cesium, although in many of their properties they are closer to potassium; the salts of thallium have values of $K_{cr.}$ close to those of cesium.

The values of $K_{cr.}$ for the fluorides are considerably higher than for the chlorides, and the values for lithium much higher than for sodium. This indicates that the coordination valence increases sharply as the atomic weight decreases in this subgroup of the Mendeleev system. This is expressed by an increase in the number and complexity of the crystalline hydrates, and in fact is of fundamental importance for the formation of crystals. Therefore, the formula, for example, of sodium chloride crystals is actually $[NaCl_6][ClNa_6]$ and for cesium chloride $[CsCl_8][ClCs_8]$.

Corresponding to this fact, the salts of uni-univalent ions, of which one ion is at an extreme (Cu, Ag) tend to have higher valences, and show a sharply increased $K_{cr.}$:

	$K_{cr.}$		$K_{cr.}$
NaCl	71000	CuCl	288000
KCl	55000	AgCl	105000.

Analogous regularities are observed for the halides of bivalent ions, but all the values are correspondingly higher, thus resulting in the insolubility in water of CaF_2, with its $K_{cr.}$ close to 250,000, and the chemical stability of MgF_2, expressed in the fact that Mg is not corroded by hydrofluoric acid, exactly as CuF_2 is also almost insoluble.

TABLE 1

Interatomic Linkage of Crystals of Uni-univalent Halides

Salt	C	d_0	$\beta = 3 \cdot a$	$K_{cr.}$
LiF	0.50	2.60	0.0_3125	227000
LiCl	0.282	2.068	0.0_3144	83200
LiBr	0.15	3.464	0.0_3162	66100
LiI	0.097	4.06	0.0_3193	42100
NaCl	0.302	2.73	0.0_3128	133000
Na	0.206	2.17	0.0_3127	72400
NaBr	0.118	2.18	0.0_3125	42000
NaI	0.0822	2.45	0.0_3141	27100
KF	0.224	2.369	0.0_3121	90400
KCl	0.162	1.986	0.0_3108	61000
KBr	0.1033	2.756	0.0_3115	50000
KI	0.0744	3.36	0.0_3111	46500
RbCl	0.106	2.76	0.0_3112	55000
RbBr	0.0704	3.36	0.0_3111	46500
RbI	0.0582	3.55	0.0_3101	42000
CsCl	0.0747	3.99	0.0_3137	42000
CsBr	0.0583	4.05	0.0_4555	35000
CsI	0.0478	4.79	0.0_3146	21000
$[NH_4]Cl$	0.363	1.53	0.0_337	31000
$[Ph_4]I$	0.103	3.02	0.0_344	18000
TlCl	0.0528	7.02	0.0_3168	48300
TlBr	0.045	7.54	0.0_3172	40600
CuCl	0.14	3.53	0.0_4354	286000
CuBr	0.089	4.72	0.0_456	155000
CuI	0.0634	5.29	0.0_467	103000
AgCl	0.091	5.57	0.0_4988	105000
AgBr	0.074	6.33	0.0_3148	73600
AgI	0.055	5.68	0.0_422	29200
Hg_2Cl_2	0.052	7.10	0.0_3103	74000
HF (at 92°)	0 435	0.991	0.0_369	14000

On the other hand, during the transition to the halogen compounds of the tri- and tetravalent ions, except for La^{+++} (and probably the remaining rare earths) and Fe^{+++} (probably also Cr^{+++} and Mn^{+++}) a decrease is observed (for example, with $AlBr_3$ and AlI_3, $K_{cr.}$ is very small). In compounds of all the remaining tri- and tetravalent elements, $K_{cr.}$ is of the order of 10,000 to 20,000 atmospheres, except for $SiCl_4$, (but in this case the value of $K_{cr.}$ has been calculated not for 0° but for 80°) and for $ZrCl_4$, $ThCl_4$, and UCl_4, which give salts relatively difficult to hydrolyze.

We must note that the relatively high values of $K_{cr.}$ for $ZrCl_4$, $ThCl_4$, and UCl_4 force us to recall also the very high stability of ZrO_2, ThO_2, UO_2, expressed in the high melting points of ZrO_2, 3060°; $ThCl_2$, 2680° (the melting point has not been determined for UO_2, but for UO_4 it is about 2200°).

In this connection we must also note that those halides which have $K_{cr.}$ above 20,000 can be obtained from aqueous solution in anhydrous form, provided their ions are univalent. Those which have $K_{cr.}$ above 100,000, and bivalent cations, can be obtained from aqueous solutions anhydrous or hydrated, like those whose cations (Fe, La, and the rare earths) do not transform into stable anions. Anhydrous crystals both of the uni-univalent salts, as well as of the bi-univalent,

TABLE 2

Interatomic Linkage of Crystals of Bi-univalent Halides

Salt	C	d_o	$\beta = 3 \cdot \alpha$	$K_{cr.}$
$BeCl_2$	0.181	2.32	0.0_474	166000
MgF_2	0.263	3.13	0.0_432	531000
$MgCl_2$	0.18	2.32	0.0_474	116000
CaF_2	0.237	2.11	0.0_4543	249000
$CaCl_2$	0.169	2.22	0.0_467	182000
CaI_2	0.0592	3.96	0.0_491	53000
$BaCl_2$	0.0896	2.63	0.0_460	84300
ZnF_2	0.181	4.70	0.0_434	313000
$ZnCl_2$	0.136	2.93	0.0_487	94200
$ZnBr_2$	0.033	3.64	0.0_489	70000
CdF_2	0.124	6.10	0.0_3080	195000
$CdCl_2$	0.0937	4.05	0.0_3073	109000
CdI_2	0.0513	5.64	0.0_3107	55700
HgI_2	0.0395	6.28	0.0_3072	74000
$PbCl_2$	0.0657	5.91	0.0_309	88000
$PbBr_2$	0.0533	6.61	0.0_309	80700
PbI_2	0.0427	6.13	0.0_4108	50000

TABLE 3

Interatomic Linkage of Crystals of Tri-univalent Halides

Compound	C	d_o	$\beta = 3 \cdot \alpha$	$K_{cr.}$
$AlCl_3$	0.193	2.41	0.0_3060	160000
$AlBr_3$	0.0958	2.54	0.0_3283	18000
AlI_3	0.061	2.63	0.0_3202	17000
$LaCl_3$	0.099	3.89	0.0_3048	165000
$FeCl_3$	0.156	2.80	0.0_306	150000
PBr_3	0.0944	2.85	0.0_357	10000
PI_3	0.062	3.55	0.0_343	11000
$AsCl_3$	0.141	2.16	0.0_339	16100
$AsBr_3$	0.08182	3.66	0.0_342	14600
AsI_3	0.0561	4.39	0.0_348	12700
$SbCl_3$	0.0116	3.06	0.0_3239	30000
$SbBr_3$	0.0704	4.15	0.0_331	19500
SbI_3	0.0509	4.85	0.0_321	24300
$BiCl_3$	0.0762	3.89	0.0_328	22000
$BiBr_3$	0.057	4.75	0.0_327	20700
BiI_3	0.043	4.96	0.0_321	20900
PCl_3	0.018	3.01	0.0_350	54700
$POCl_3$	0.16	1.69	0.0_338	14700
$POBr_3$	0.101	2.82	0.0_328	20200

are obtained the more easily the greater the atomic weight of the cation. But the production of anhydrous chlorides, bromides, and iodides of Be and Mg from aqueous solution is of considerable difficulty because of hydrolysis.

As I have demonstrated several times previously ("The Chemistry of Colloids and Gels", 1925; "Physical Chemical Theory", 1930) the solution of halides in water is a complicated phenomenon, consisting of at least three processes:

TABLE 4

Interatomic Linkage of Crystals of Tetra-Univalent Halides

Compound	C	d_0	$\beta = 3 \cdot \alpha$	$K_{cr.}$
$SiCl_4$ (at 79°) ...	0.13	1.48	$0.0_3 55$	36000
$SiBr_4$	0.092	2.81	$0.0_3 51$	10500
SiI_4	0.059	3.9	$0.0_3 48$	10000
$TiCl_4$	0.111	1.76	$0.0_3 167$	46000
$TiBr_4$	0.081	3.72	$0.0_3 283$	22000
TiI_4	0.0539	4.55	$0.0_3 222$	22800
$GeCl_4$	0.15	1.88	$0.0_3 68$	11200
$SnCl_4$	0.123	2.28	$0.0_3 46$	12000
$SnBr_4$	0.073	3.35	$0.0_3 57$	8900
SnI_4	0.059	4.70	$0.0_3 52$	9500
$ZrCl_4$	0.126	2.80	$0.0_4 89$	65000
$ThCl_4$	0.0788	4.59	$0.0_3 30$	241000
UCl_4	0.0941	4.85	$0.0_3 40$	171000
UCl_6	0.115	3.52		

1) The hydration of the surface of the ions of the salt with formation of ions more completely hydrated as their ionic valence is higher and their atomic weight lower.

2) The diffusion of water through aqueous canals between the hydrated ions toward the dense network behind them, and the hydration of the ions of the latter, leading to swelling.

3) The breaking off of the ions into the water because of the attraction of the hydrating water for the water of the solvent, with simultaneous hydrolysis of the salt as a result of ionic interchange, the process appearing as hydrolysis.

For uni-univalent ions, the process takes place approximately in conformity with this scheme. In the case of salts of polyvalent ions, the latter, as they pass into the solution, can immediately form polyions, as for example:

$$BiCl_3 + 3H(OH) \rightleftarrows Bi(OH)_3 + 3HCl$$

$$nBi(OH)_3$$

$$n\left\{H^+ \ldots {}^{-}[HBiO_2]^+ \ldots OH^-\right\}$$

$$(n-1)H(OH) + HO\left\{{}^{-}[HBiO_2]^+ \ldots {}^{-}[HBiO_2]^+\right\}OH^-$$

The polyamphions easily form crystalline polyions and polyamphions which precipitate out. Consequently, in the case of sufficiently high valence of the ions, the process of reaction of the halide takes place in several steps:

A – hydration of the ions,

B – swelling of the surface layer of the crystal,

C – hydrolysis,

D – polyamphion formation,

E – crystallization of the polyamphions.

In the case of uni-univalent ions, processes D and E are missing. In case one ion is univalent and consequently cannot form polyions and crystalline polyions, the salt is easily drawn into the water. On the other hand, in contact

with water, the polyvalent ions undergo polyamphion formation with extreme ease and readily form crystalline polyamphions. This takes place with especial smoothness when an acidified concentrated solution of $Bi(NO_3)_3$ is diluted with water, and results in the precipitation of a basic salt.

Thus, although in actual fact any salt undergoes hydrolysis during solution in water, because an ionic interchange of the salt with water cannot help taking place:

$$K^+Cl^- + H^+(OH)^- \rightleftarrows H^+Cl^- + K^+(OH)^-$$

however, because of the equality of the number of microvolumes of alkali (KOH) and acid (HCl), it seems, to litmus, for example, as if no hydrolysis has taken place. None the less, investigation permits us to ascertain that the introduction of a salt of uni-univalent ions (KCl, NaCl) easily acidifies water, even when the salt is introduced in the course of work in colloid chemistry. The cause of the production of acidity depends on the fact that the H^+ ion is more mobile than the OH^-, and in a given time the reaction

$$\underset{|}{H}Cl + \underset{|}{H}(OH) \rightleftarrows \underset{|}{H}Cl + \underset{|}{H}(OH)$$

takes place more often than

$$K(O\underset{|}{H}) + H(O\underset{|}{H}) \rightleftarrows K(O\underset{|}{H}) + H(O\underset{|}{H}).$$

Hence, the acidity that results when KCl is introduced into a solution. Even if the valences of the ions are not equal, as with $AlCl_3$, $Fe_2(SO_4)_3$, etc., and the amphoteric properties of one of the ions are more pronounced, that part of the ions which forms polyions is reduced in number because of the formation of polyions and especially of crystalline polyamphions or polyions. Then the hydrolysis (of $AlCl_3$, $Fe_2(SO_4)_3$, Na_2CO_3, Na_3PO_4, etc.) obviously takes place, occurring instantaneously in the case

$$SnCl_4 + 4H(OH) \rightleftarrows Sn(OH)_4 + 4HCl.$$

Thus, hydrolysis, as an interchange of the ions of the salt with the ions of the water, takes place in the solution of any salt; obvious hydrolysis, that is, observable by its deviation from pH 7, is possible if the ions of one charge more easily form stable polyions (and crystalline polyions) than the ions of the other. But crystalline polyions are formed more often and are more stable the higher the valence of the ions. Hence, the rule that hydrolysis (deviation from pH 7 and formation of a gel-like or colloid precipitate) takes place more obviously the greater the difference between the valences (both ionic and coordination) of the ions of the salt.

We must note at the same time that the higher the ionic valence of the ion, the more strongly do the anionic properties show themselves in the form of hydrates, i.e., the less the tendency to add additional electrons without giving up their own.

In fact, with Na(OH) the tendency to give up H^+ is shown only in a strongly alkaline medium in the reaction $Na(OH + H)NaO \rightleftarrows H(OH) + Na_2O$; $Zn(OH)_2$ dissolves in alkali, and $Mg(OH)_2$ readily gives crystalline polyions of the type of Sorel cement; for Al^{+++} and Si^{++++}, the formation of anions is still more characteristic. CCl_4 is a limiting transition case which resembles CH_4 (in the same way that LiH resembles LiCl). But in CCl_4 the carbon exchanges its four electrons with the four hydrogens because on the one hand the ionic properties are very weak (despite the fact that salts of methane, like aluminum carbide, are prepared in considerable quantities), and on the other there is a tendency to form methyl compounds with metals [$Mg(C_2H_5)_2$, $Zn(C_2H_5)_2$] almost identical with the tendency to form compounds with halogens. However, because of the great tendency of $Mg(OH)_2$ and $Zn(OH)_2$ to form crystalline polyions, the stability of these first compounds,

TABLE 5

Relation Between Interatomic Linkage and Melting Point

Compound	T_m	$K_{cr.}$	$T_m/K_{cr.}$	Compound	T_m	$K_{cr.}$	$T_m/K_{cr.}$
LiF	1074	227	4.4	CdI_2.....	660	55.7	12
LiCl ...	873	83.2	11	HgI_2.....	1626	74.0	8.4
LiBr ...	820	66.1	15	$PbCl_2$....	723	88.0	8.3
LiI	726	42.1	1.7	$PbBr_2$ ...	643	80.7	8
NaF	1270	133	9.0	PbI_2	666	50.0	13.3
NaCl ...	1073	72.4	15	$AlCl_2$ ...	563(?)	160	3.5
NaBr ...	1048	42.0	25	AlI_3	464(?)	17.0	27
NaI	933	27.1	35	$LaCl_3$ ...	063	165.0	6.4
KF	1110	90.4	12	$FeCl_3$ ...	575	150.0	3.0
KCl	1063	61.0	17	$PbBr_2$ ...	213	10.0	21.3
KBr	1030	50.0	21	PtI_2	334	11.0	3.0
KI	960	46.3	20	$AsCl_3$ ...	260	16.1	1.6
RbCl ...	999	55.0	19	$AsBr_3$ ...	304	14.6	20
RbBr ...	956	46.5	20	AsI_3	414	12.7	30.2
RbI....	915	42.0	22	$SbCl_3$ ...	346	30.0	10.5
CsCl ...	919	92.0	22	$SbBr_3$ ...	367	20.0	18
CsBr....	900	35.0	26	SbI_3	344	24.3	23
CsI	894	21.0	42	$BiCl_2$ ...	616	22	28
TlCl ...	702	48.3	16	$BiBr_3$ ...	490	21	23
TlBr ...	723	40.6	18	BiI_3	700(?)	21	33.(?)
CuCl ...	898	28.6	23	PCl_3	476	54.7	8.7
CuBr....	753	155	4.9	$POCl_3$ ...	275	14.7	18
CuI....	929	103	9.0	$POBr_3$ ...	328	20	16
AgCl ...	728	105	6.9	CCl_4	250	9.7	25
AgBr....	695	73.5	9.4	CBr_4	363	9.6	37
AgI	825	29.2	9.4	$SiCl_4$ ...	204	36	6.0
Hg_2Cl_2 .	816	74.0	28	$SiBr_4$ ...	478	11	25
HF	161	14	12	SiI_4	394	10	39
$BeCl_2$ ..	1058	166	6	$TiCl_4$ ...	250	46	23
MgF_2 ...	991	531	1.8	$TiBr_4$ ...	312	22	14
$MgCl_2$ ..	1058	116	8.8	TiI_4	430	5.4	19
CaF_2 ...	1651	249	6.5	$GeCl_4$ ...	272	11	22
$CaCl_2$ ..	1047	182	5.9	$SnCl_4$ ...	260	12	22
CaI_2 ...	1013	52	20	$SnBr_4$ ...	303	9	34
$BaCl_2$ ..	1033	84	12	SnI_4	417	9.5	44
$ZnCl_2$ ..	638	94.2	6.7	$ZrCl_4$ ...	620	65	9.5
$ZnBr_2$...	667	70.0	9.5	$ThCl_4$ ...	1050	240	43
CdF_2 ...	841	195	4.2	WCl_6	548	29	18
$CdCl_2$ ..	1373	109	12				

like $Zn(CH_3)_2$, is also less in the presence of water than the stability of CH_3Cl, CH_2Cl_2, etc., despite the fact that there are no halogen derivatives of hydrocarbons which would not undergo hydrolysis. It is clear, however, that because of the almost symmetrical electron exchange of carbon with hydrogen, the bond excludes or almost excludes an ionic exchange between neighboring particles, and by virtue of that fact even crystals of the compounds of halogens with atoms of higher valence have near 0° a low interatomic linkage (of the order of 10,000 to 15,000 atm.). The halogen hydrides in a free state are very weakly ionized, and in conformity with the low value of their ionizing tendency, that is, with

the approximate symmetry in the gaseous state of each of its atoms with exchangeable electrons, $K_{cr.}$ for hydrogen fluoride H-F is very low (14,000 atm., at about -100° at that).* There is no doubt that in solution F^- and Cl^- ions are hydrated, and moreover, in such a manner that hydroxyls are attracted toward them, a fact which, corresponding with the structure of the acids $H_2[Pt(OH)_6]$ and $H[Au(OH)_4]$, confirms the anionic properties that are produced in H+ in water solutions with cationic properties.

Thus, the differences between halogen salts which do not easily permit the observation of hydrolysis, and acid anhydrides, are dependent both upon inner causes (the symmetry of the tendency to hold exchangeable electrons both upon the central atom and upon the halogen attracted to it) and upon external causes, i.e., the greater the ease of formation of crystalline polyamphions, the higher the valence of the ions (central ions, in these halogen compounds).

We must still verify the relation between the force opposing thermal expansion, i.e., $T_{cr.}$, and the value of the energy necessary for the destruction of the crystal network (T_m). The data are compared in Table 2. From this it is clear than uni-univalent, tri-univalent, and tetra-univalent salts have values of the ratio $T_m/K_{cr.}$ averaging close to 20, while salts of the bi-bivalent, and tri-univalent type which are difficult to hydrolyze, have on the average values one-third this.

Thus, the temperature stability of the crystals of halogen compounds, including bivalent ions and Cu^+ and Ag^+, is low with regard to $K_{cr.}$ in comparison with the same ratio $T_m/K_{cr.}$ for uni-univalent, tri-univalent, and tetra-univalent compounds.

In other words, the stability of the network of the former compounds decreases with the temperature more rapidly than that of the latter. The highest value of the ratio $10^3\ T_m/K_{cr.}$ calculated (For SnI_4) is 44, the lowest, for $AlCl_3$, is 3.5. The average is close to 17, i.e., the limits of variation are not very great.

Thus, the fluoride salts MgF_2 and CuF_2, which are insoluble and react with difficulty with water, have $K_{cr.}$ higher than 250000 atm. The rest of the halogen compounds investigated are either soluble in water or easily react with it, like the acid anhydrides, and have $K_{cr.}$ below 100,000 atm. Of these, the difficultly soluble ones (CuBr, CuI, AgCl, AgBr, AgI, HgCl, HgI_2, $PbCl_2$, $PbBr_2$) have $K_{cr.}$ above 75,000, but PbI_2, CdF_2, and AgI must be excluded because in their case extrapolation is not sufficiently reliable. Statistically, we are impelled to conclude that an increase of $K_{cr.}$ above 75,000 atm. leads to very little solubility in water.

SUMMARY

1. The value of $K_{cr.}$ falls sharply for alkali halide salts during the transition to the heavier cations. The smallest values calculated are for the ammonium salts.

2. The value of $K_{cr.}$ for a given halogen falls from Li^+ to Na^+, passes through a maximum at K^+, and falls again toward Rb^+ and Cs^+.

3. Halogen compounds of $[NH_4]^+$ have very low values of $K_{cr.}$

4. $K_{cr.}$ for CuCl, CuBr, CuI, AgCl, AgBr, Hg_2Cl_2 is large, corresponding to their low solubility and the high coordination tendency of their cations.

5. $K_{cr.}$ for bi-univalent salts falls with a decrease in the atomic weight of the halogen, and reaches its highest value with MgF_2 and CaF_2.

*We must recall that even water, cooled to -78° is very mobile, that is, that both K_1 and its ionizing tendency are very small.

6. $K_{cr.}$ for tri-univalent and tetra-univalent compounds which easily undergo hydrolysis is in general very low, except for $AlCl_3$, $LaCl_3$, $FeCl_3$, and probably $CrCl_3$ and $MnCl_3$.

7. The process of solution of halogen compounds consists of: a) the hydration of the surface ions; b) the swelling of the surface and subsurface dense network; c) hydrolysis; d) polyamphion formation during the passage of the cations into solution, if their ionic valence is higher than unity or their coordination valence is very large; e) crystallization inside of the polyamphions or formation of crystalline polycations corresponding to the polycations, with transition to colloidal solutions.

8. It is necessary to distinguish between the hydrolysis of salts which always takes place during solution and is sometimes observed only by virtue of the slight change in the value of pH, the action on indicators, etc., and the hydrolysis which depends on polyion formation or on the formation of crystalline polyamphions, and is made evident by a sharp change in pH.

9. The ratio $T_m/K_{cr.}$ varies within relatively narrow limits (about 22 for uni-univalent, tri-univalent, and tetra-univalent ions and about 7 for bi-univalent compounds), i.e., it is close to being constant.

10. The solubility of salts falls sharply if $K_{cr.}$ is above 100,000 atmospheres, and especially sharply (almost to zero) if $K_{cr.}$ is above 250,000 atm.

11. Typical acid halides have $K_{cr.}$ below 30,000.

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THE OPTICAL PROPERTIES AND STRUCTURE OF POLYIODIDES*

D. A. Godina and G. P. Faerman

Chemical and Optical Properties of Compounds of Iodine with Quinine

1. About a hundred years ago the English chemist Herapath observed that the action of alcoholic solutions of iodine on a solution of quinine bisulfate gave fine, tiny, shining crystals, later called herapathite.

This compound attracted attention because of its extraordinarily strong pleochroism – stronger even that that of tourmaline.

Detailed chemical investigations of herapathite were carried out by Jorgensen. He found that quinine sulfate forms with iodine not one, but several compounds, which are distinguished from each other in composition, color, and crystal form.

In all, he observed seven compounds, of which four were stable. These had the composition $4Quin, 3H_2SO_4, 2HI, I_n, \underline{x}H_2O$. The other three, less stable, had the composition $2Quin., H_2SO_4, 2HI, I_n$.

All these compounds had sharply expressed pleochroism, and differed in the colors which were produced in their crystals when viewed in polarized light and were dependent only on the number (n) of molecules of iodine which entered into the composition of the given modification.

Thus, Jorgensen, in contradistinction to Herapath and his other predecessors, believed that in addition to quinine, iodine, sulfuric acid, and water, hydriodic acid also entered into the composition of herapathite. This question was subjected by us to a special investigation [1]. We found that in the absence of iodide ions, the reaction for the formation of herapathite does not, in general, take place.

Actually, if a solution of quinine bisulfate is mixed with a freshly prepared solution of iodine in ethyl alcohol, at first no crystalline precipitate is formed at all. But in the course of time, little by little, there begins a slow separation of crystals of herapathite. The formation of herapathite can be considerably speeded up by the addition to the solution of hydriodic acid or potassium iodide.

It was noted that the formation of herapathite takes place much more rapidly if the alcoholic solution of iodine is used after being allowed to stand for some time or is subjected to a preliminary heating.

It is known that in alcoholic solutions of iodine a partial reduction of

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*Read June 17, 194 at a session of the Leningrad Section of the Mendeleev All-Union Chemical Society.

the iodine to HI takes place.

Using analytical methods, we followed the accumulation of iodide ions in the course of time in iodine-alcohol solutions both at room temperature and on heating, and found a complete parallelism between the velocity of formation of the crystals of herapathite and the iodide content of the solution. This accumulation of iodide explained the above-mentioned gradual separation of herapathite crystals from the solutions which when poured together produced no rapid formation of a precipitate. The introduction into the alcoholic iodine solution of substances capable of reducing the iodine with the formation of hydriodic acid (for example, acetone) also considerably speeded up the precipitation of herapathite.

Thus, it was shown that iodide ions are necessary participants in the reaction for the formation of herapathite crystals. They can be introduced into the reaction zone in the form of hydriodic acid or its salts, or they can be produced by reduction of the iodine in alcoholic solution, especially by heating, by long standing, or by the addition to the solution of substances capable of reducing the iodine.

2. The very fact that iodide ions were necessary for the reaction led to the idea that the entry of the iodine into the molecule of the substance being formed takes place in the same manner as in the formation of polyiodides. It is known that iodine, of all the halogens, has the greatest tendency to form polyhalide compounds. The formation of the complex polyhalide ion I_3^- in the reaction between iodine and potassium iodide has been well studied. It is also known that in the case where more than a single iodine molecule is attached to a single iodide ion, the amount of iodine forming part of the polyhalide compounds is variable, depending on the excess of iodine at the moment of formation of the compound and not being determined by stoichiometric laws.

The stability of the polyhalides increases from fluorine to iodine parallel to the increase in the polarizability of the halogen molecules, and also to the increase in the ionic radius of the cation forming the polyhalide salt. The stability of the bond of the iodine molecules in the polyiodide decreases with the increase in the number of added iodine molecules. Heating of the polyiodide favors the splitting off of iodine, which takes place the more readily the greater the number of iodine molecules in the compound. The majority of polyiodides have extremely low solubility, which increases with the increase of the dielectric constant of the solvent. They often contain water of crystallization, which cannot be removed without decomposing the compound. At the same time, under the action of water, the polyiodide is in many cases decomposed with the separation of free iodine.

Herapathite has all these properties of the polyiodides. In investigating the reaction in which herapathite is formed, we found that the iodine has a tendency to enter into this compound in the most varied amounts, both in the process of forming the different modifications of herapathite as well as when adding subsequently to already formed crystals. But the amount of iodine which can enter a compound has a definite limit, and cannot exceed two molecules per molecule of HI.

Our experiments did not confirm Jorgensen's claim that there were definite stoichiometric relations between the amounts of iodine and of hydrogen iodide characteristic for each modification of herapathite. Although the modifications of the colors of the crystals as described by Jorgensen actually exist, the transition from one to another is accompanied by a continuous change in the amount of iodine, and can be accomplished by adding iodine to, or taking it away from, already formed crystals, which do not change their shapes in the process. All this gives us reason to assume that the modifications of herapathite isolated by Jorgensen were not individual compounds.

Herapath had already observed that not only quinine but cinchonine, quinidine, and other members of the quinine alkaloid family as well, formed compounds similar to herapathite. Jorgensen showed that this type of compound was formed not only with alkaloids, but also with many inorganic complexes of cobalt and platinum. These complexes formed compounds which contained, like herapathite, for four molecules of the complex three molecules of sulfuric acid and a varying number of iodine molecules. These compounds were essentially similar to herapathite both in crystalline form and in the value of their pleochroism.

It is obvious that the properties of the compounds formed in all the cases described have nothing to do with the chemical nature of the quinine, cobaltammine, or other substances which form the complex cation of the compounds. The great volume of the cation in these cases has no more significance than that it favors the formation of a stable polyiodide with a large number of added molecules of I_2. Moreover, upon heating or treatment with water, these compounds decompose like the usual polyiodides.

All the compounds similar to herapathite are very slightly soluble in polar solvents and completely insoluble in non-polar liquids. Thus, we may say with certainty that herapathite is a typical polyiodide.

3. The pleochroism of herapathite is both a specific property and unusual in magnitude, and it is this particular property of herapathite which is responsible for the great interest which it has aroused for almost a hundred years. All pleochroism owes its origin to the difference in absorption in a region of the spectrum for the "ordinary" and "extraordinary" rays which arise when light is passed through an anisotropic medium, and in consequence, for a given part of the spectrum, in the value of the absorption of these rays.

Pleochroism exists in very many crystalline substances and compounds. In most of these, differences in the position of the absorption bands for the ordinary and extraordinary rays, like the difference in the coefficients of absorption, are not great. With herapathite, the absorption bands are displaced almost the entire region of the visible spectrum, and a crystal thickness of 0.2 to 0.3μ absorbs the "ordinary" ray almost completely (Fig. 1).

As both the value of the pleochroism and the color of the crystals of the different modifications of herapathite depend on the amount of iodine added, and investigation of the relationship between the amount of iodine and the optical properties of the compounds formed may shed some light on the causes of the formation in herapathite of such an unusually high degree of pleochroism.

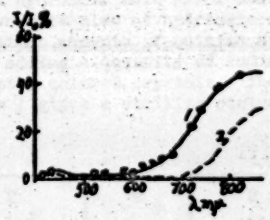


Fig. 1. Transmission spectra of the "lilac" (1) and the "blue" (2) suspensions of herapathite.

We shall characterize the spectral absorption of the "ordinary" ray in crystals of herapathite by the color observed when the planes of polarization of the crystal and the analyzer intersect.

The chief modification of herapathite, which has, according to Jorgensen's data, the composition: $4Quin, 3H_2SO_4, 2HI, 2I_2, xH_2O$, has, under these conditions a blood red color, i.e., it absorbs all the rays of the visible spectrum beyond the orange and the red. Upon further addition of iodine, the color becomes, in sequence, purple, lilac, and finally blue. Further addition of iodine leads to a black color.

If we look at the crystals of herapathite while their planes of polarization are maintained parallel to that of the analyzer, then all the modifications of herapathite, excluding the black, will seem almost colorless. Even the crystals of the black modification under these conditions will have a pale yellow color. This color, apparently, can be explained by the presence of excess iodine, which does not enter into the composition of the compound, and it becomes stronger the greater the excess of iodine. If iodine is gradually removed from the compound, a series of changes in the color of the crystals is observed in the reverse order from black to red.

The crystals of herapathite are extremely fine; therefore the investigation of the optical properties of separate small crystals, the measurement of their spectral absorption, and even the visual estimation of the color as the composition is changed, present considerable difficulties, and are often completely impossible. On the other hand, the dilute suspensions of microcrystals of herapathite have very definite colors, and are very sensitive to the slightest change in the concentrations of the substances reacting.

This property of the suspensions can be explained by the fact that the tiny crystals are distributed in them at random. Thus, their planes of polarization intersect in many ways, and the total absorption is strengthened, in consequence of which fact the color becomes more intense and its modification more noticeable. Having visually observed the color of such a suspension, we can very accurately note the slightest change in it when the conditions of reaction are changed. Microcrystalline suspensions of herapathite are obtained when very dilute solutions of quinine bisulfate and mixtures of iodine and HI are poured together in the presence of small amounts of collodion, which plays the role of a protective colloid; during this process, the solvent is stirred, to lower the solubility of the herapathite.

The investigations we carried out on the relationship between the color of the crystals of herapathite obtained and the quantitative proportions of the substances reacting with each other showed that the color of the crystals depended not so much on the absolute amount of iodine present in the reaction zone as on the ratio of the amounts of iodine and iodide. We found that in the formation of herapathite, the amounts of quinine and hydriodic acid which combined were in definite stoichiometric proportions. Two molecules of hydriodic acid added to four molecules of quinine. Taking constant amounts of quinine and hydriodic acid corresponding to this ratio, and adding a quantity of iodine, it was possible to obtain by this reaction differently colored crystals. Their color depended on the ratio of $[I_2]/[HI]$. Table 1 gives a striking picture of the results of these experiments.

TABLE 1

Quinine/HI	2	2	2	2	2
I_2/HI	1	1.25	1.50	1.75	2.00
Color	Red	Purple	Lilac	Blue	Dark blue

Keeping the proportions of quinine and iodine constant and decreasing the amount of HI taking part in the reaction, we obtained a series of colors from red to dark blue in the order shown in Table 1.

This means that the iodine can unite with the quinine only through the HI, by adding to the iodide ion, i.e., by forming a polyiodide. When there are more than two molecules of quinine to a single molecule of HI, then in general the excess of quinine does not react, uniting neither with the HI nor with the

iodine. An excess of iodine equivalent to the quinine enters into reaction, forming a compound with a greater I_2/HI ratio than when the amount of Hi is less. This also explains the series of color changes of the crystals that has been noted above; during this process, of course, the total amount of herapathite formed is correspondingly decreased.

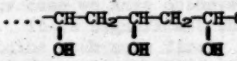
If the amount of hydriodic acid entering the reaction zone exceeds that needed for the ratio: 2 mols of quinine per mol of HI, then the amount of HI in excess of the equivalent enters into reaction with the iodine, forming HI_3, in consequence of which the amount of iodine entering into the composition of the simultaneously formed herapathite is decreased. Consequently, an increase in the amount of HI taking part in the reaction, or the addition of HI or KI to the suspension of herapathite crystals, can cange the color of the suspended crystals from dark blue to red, and even completely decompose the herapathite.

It should be noted that the change in color of the herapathite suspension during the change in the value of the I_2/HI ratio takes place continuously, and therefore cannot serve as an index of the entrance of the iodine into the composition of the herapathite in definite stoichiometric amounts.

Chemical and Optical Properties of Compounds of Iodine With Polyvinyl Alcohol and Starch

4. During recent years it has been observed that polyvinyl alcohol films impregnated with a solution of iodine in potassium iodide and subjected to vigorous stretching, aquire strongly expressed pleochroism [2].

This is one of the few polymolecular compounds which are highly soluble in water and insoluble in organic solvents. Staudinger suggests for it the formula:



This compound appears as a white powder which dissolves upon heating in water and forms a transparent, colorless and chemicaly stable sol with typical lyophilic properties. Upon evaporation of the aqueous solutions, polyvinyl alcohol forms a film which has great elasticity and stability.

Upon interaction with solutions of iodine in potassium iodide, the solutions of polyvinyl alcohol acquire an intense blue color. This reaction proceeds only in concentrated solutions of polyvinyl alcohol and does not take place in dilute solutions. Upon heating, the blue color disappears, changing to a weak yellow, and reappears upon cooling.

In the absence of potassium iodide, iodine and polyvinyl alcohol do not form a blue compound. When added in the form of an alcoholic solution to a solution of polyvinyl alcohol, the iodine colors it brown, changing to blue either upon further standing or upon the addition of potassium iodide to the solution. The addition of an excess of potassium iodide first changes the blue color of the solution to violet, and then coagulates the sol.

The color of the polyvinyl alcohol sol containing iodine, like the color of the herapathite crystals, depends essentially on the ratio of the amounts of iodine and iodide added. This is clearly evident from Table 2.

In this case, as during the formation of the herapathite, the presence of iodide ions considerably speeds up the process. When the concentration of potassium iodide is fairly great, the blue color is intensified manyfold. The formation of one or another color of the polyvinyl alcohol sol depends on the same causes as the colors of the herapathite crystals. In the absence of potassium

iodide, polyvinyl alcohol does not react with iodine, and the sol is colored brown. After a time, depending on the formation of HI as a result of the reduction of iodine, a small quantity of the blue compound is formed. The mixture of colors of the excess iodine and this compound composes the green color. As the concentration of KI added is increased, as a result of the speeding up of the reaction, the green color appears more rapidly, turning in time to blue. When sufficient KI is added, the blue color forms as soon as the solutions are mixed. In aqueous solution we did not observe a violet color of the sol, but it was clearly observed in polyvinyl films upon impregnating their solutions with suitable concentrations of iodine and potassium iodide.

Thus, the reaction of polyvinyl alcohol with iodine fairly accurately repeats the reactions observed during the formation of herapathite, in particular, when the polyvinyl alcohol forms a film. This gives us reason to consider that the compound of iodine with polyvinyl alcohol is also a polyiodide.

TABLE 2

I_2/HI	Color after mixing	Color after 3 hours	Color after 1 day
I_2 alone	brown	green	green
10:1 ...	brown	green	blue
10:2 ...	green	green	blue
10:5 ...	blue	blue	blue

5. As has already been observed, stretching of the polyvinyl alcohol film which has been impregnated with iodine produces considerable pleochroism; during this process, a sharp change in color takes place. The blue film turns gray-green, and the intensity of the color is at the same time considerably decreased.

It is known that the stretching of films of various polymers produces in them double refraction, as a result of the orientation of the micelles forming them. In our case we have observed a phenomenon apparently related to this orientation. It is significant that the stretched film of polyvinyl alcohol holds the iodine much more firmly than the unstretched. This is evident in the increased thermal stability of the color and the increase in stability with regard to the action of solvents for iodine.

Stretching of the film of polyvinyl alcohol, resulting in mechanically oriented micelles, at the same time influences the character of the reaction of the film with iodine and considerably hastens the addition of iodine to the polyvinyl alcohol. Polyvinyl alcohol films impregnated with a solution of iodine with a low potassium iodine content are colored brown, and turn blue only after some time. If such a brown film is stretched, the gray-green color is considerably strengthened, and the film becomes pleochroic. Upon cessation of the stretching, the film contracts. During this process, however, the original brown color does not return, but a blue is formed, such as is obtained by adding to the film a solution of iodine with a sufficient content of potassium iodide. Thus, stretching of the film so to speak substitutes for an insufficiency of potassium iodide, speeding up the addition of iodine. The reversible change of color of the film from blue to gray-green, and the formation or disappearance during this process of the pleochroism, clearly indicate the action of the orientation factor. The disorientation of the micelles upon cessation of the stretching is accompanied by the appearance of the blue color. This effect is entirely similar to the formation of color in a suspension of herapathite as a result of the mutual intersection of the planes of polarization of crystals oriented at random in the suspension.

6. The blue color obtained by the reaction of polyvinyl alcohol with iodine is entirely similar to the color obtained in the well-known iodine-starch reaction. The chemical closeness of starch and polyvinyl alcohol forces us to suppose that this color may be produced by one and the same group of causes.

Over a period of almost a century and a half the iodine-starch reaction has been studied by a formidable number of investigators [3,4]. None the less, up to the present time this reaction cannot be considered as completely investigated. It is known that upon the addition of small amounts of iodine to the starch solution an intense blue color is produced. Attempts to determine stoichiometric relations between the iodine and the starch in the formation of the compound have not been crowned with success.

It has been shown that the quantity of iodine bound to the starch depends on the concentration of iodine in the solution. However, there is a limit to the amount of iodine that can be bound. Addition of an excess results in the conversion of the blue color to a green one.

The question of the role of the iodide ion in this reaction also remains unclear at present. Several authors believe that in the absence of iodide the iodine is bound to the starch weakly, and that the essential role in this reaction is played by the ion I_3^-. Others assume that the presence of iodide merely stimulates the reaction, which would also take place without it. However, an increase in the concentration of iodide stimulates the iodine-starch reaction only up to a certain point. Upon addition of an excess of iodide, the blue color is transformed into a purple and a red one. A change of color from blue to yellow, via violet, purple, and red, can be produced by heating the sol. This process is completely reversible. This sort of reversible change of color from blue to yellow, and that in the reverse direction across the same intermediate stages, can be produced by carefully removing or adding iodine. It has been shown that the color of the iodine-starch compound is greatly influenced by the ratio of the concentrations of iodine and potassium iodide in the solution.

Rundle and his coworkers [5] during the past years have published a number of investigations of the compounds of iodine with starch, in particular, investigations of the optical properties of these compounds. They found that they could observe the formation of pleochroism during the passage of the colored starch-iodine sols through a capillary. Pleochroism was also found in the compounds of iodine with crystalline amyloses which were constituent parts of the starch.

It is not difficult to see that both the chemical and the optical properties of the compound of iodine with starch are completely similar to the properties of the compounds of iodine with polyvinyl alcohol, with quinine bisulfate, cobalt chloropentammine, cellulose hydrate, cholic acid, the hydrosols of lanthanum hydroxide and praseodymium acetate, and a number of other substances which give blue colors with iodine.

The general nature of the observed phenomenon indicates the identity of the chemical nature of the compounds formed in all these cases and permits the assumption that all these substances of considerably different types are polyiodides differing only in their cations.

The chemical behavior and optical properties of these compounds are determined chiefly by the polyiodide anion, while the chemical nature of the cation is almost a matter of indifference. It is important only that the volume of the cation be large. The larger it is, the more stably the iodine is held in the compound.

The Absorption Spectra of Herapathite and Iodized Polyvinyl Alcohol

7. A study of the absorption spectra of the polyhalides considered above may give a key to the understanding of the production of the color phenomena and pleochroism.

Fig. 1 gives the curves of spectral transmission obtained by us for a sus-

pension of the lilac and blue modifications of herapathite. From Fig. 1 it is clear that the limit of transmission of the blue modification is displaced in comparison with the red by almost 100 mμ in the direction of long wave length. The red crystals of herapathite almost completely absorb the "ordinary" ray in a large part of the visible spectrum, but all the same, the absorption of the blue crystals is somewhat greater than that of the red. The small, barely meas-

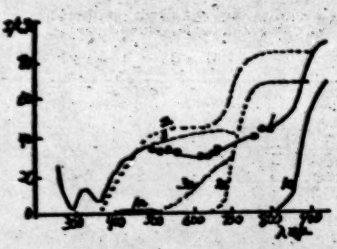


Fig. 2. Transmission spectra.

2 and 2a, "red" monocrystals of herapathite; 1 and 1a iodinated films of polyvinyl alcohol; 3 and 3a, iodine crystals of μμ thickness. Curves marked 1,2, and 3 refer to transmission of unpolarized light. Curves 1a, 2a and 3a refer to transmission through two of the objects studied, the planes of polarimtion of which intersect at an angle of 90°.

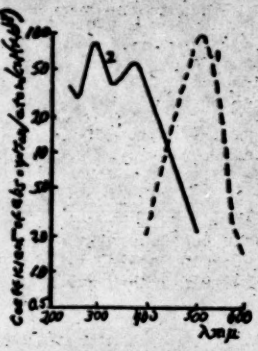


Fig. 3. Change in the coefficient of absorption of the spectrum.

1, solutions of iodine in carbon tetrachloride; 2, solutions of CsI_2 in alcohol.

urable maximum of transmission at about 500 mμ is of special interest.

In Fig. 2, alongside the transmission curves of the monocrystalline layer of the "red" herapathite, are given the curves for the spectral transmission through the iodinated and stretched films of polyvinyl alcohol. We see that in their general shape they repeat the course of the curves for herapathite, with this difference, however, that they have a small maximum of transmission in the near ultraviolet, absent in herapathite.

These curves make it possible to interpret the causes of the change in color of the crystals of herapathite and of the films of polyvinyl alcohol when the amount of iodine in them is changed.

Investigations carried out by numerous authors on the absorption spectra of iodine in different states have shown that iodine vapor has a continuous region of absorption in the visible part of the spectrum. Its maximum, in the presence of air or inert gas lies at $\lambda = 520$ mμ, and its midpoint in the interval 484 to 562 mμ. Thus, iodine vapor transmits the red and blue-violet region of the spectrum, in consequence of which it is also colored lilac [6,7].

The maximum of absorption of the solutions of iodine in nonpolar solvents lies at $\lambda = 518$ mμ, and the color is little different from the color of iodine vapor. The greater the dipole moment of the solvent, the more the maximum and the entire region of absorption are displaced in the direction of short wave length [8]. In polar solvents which form solvates with iodine, the maximum of the absorption region is displaced in the direction of short wave length by from

70 to 100 mμ, as a consequence of which these solvents are colored brown or yellow [9].

Finally, the absorption spectrum of the I_3^- ion has two maxima: about 280 and 350 mμ. The long-wave boundary of the region of absorption of I_3^- spreads partly into the visible region of the spectrum, in consequence of which compounds of the I_3^- ions are colored yellow [10].

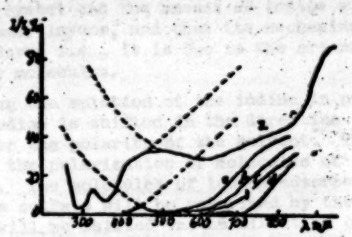


Fig. 4. Scheme showing addition of absorption spectra of complex ion I_3^- and molecular iodine, explaining the nature of the color of the herapathite crystals (1) as the amount of iodine in them is increased (a < b < c < d), and of the iodinated films of polyvinyl alcohol (2).

A comparison of the absorption spectra of iodine with the spectra of the herapathite suspensions and the films of iodinated polyvinyl alcohol permits us to assume that the absorption spectra of the latter are the result of the superposition of the spectra of molecular iodine and the ion I_3^-, as is schematically shown in Fig. 3 and Fig. 4.

This is indicated chiefly by the existence of the earlier-noted small maximum of transmission about 500 mμ. This maximum is obtained as a result of the combination of the short-wave branch of the absorption region of molecular iodine with the long-wave branch of the absorption region of the I_3^- ion.

The absorption spectrum of the iodinated and stretched polyvinyl alcohol films in the ultraviolet region fairly accurately repeats the absorption spectrum of the I_3^- ion. It has the same two absorption maxima, arranged in approximately the same manner, as the absorption spectrum of the I_3^- ion. It appears that this comparison has only a qualitative character, as no measurements have been made of the absolute absorption coefficients for polyvinyl films. In herapathite, these maxima are absent because quinine has a continuous region of absorption in the near ultraviolet part of the spectrum.

An investigation of the absorption spectra of individual crystals of herapathite, carried out in our laboratory by L.P.Churaev, showed that in this case there was a sharp departure from the Lambert-Beer law. To a certain degree of approximation it may be said that there is an inverse proportionality between the absorption coefficient and the thickness of the crystal. This may be explained by the fact that the chief mass of the crystal hardly absorbs light, or absorbs it extremely weakly, while the surfaces of the crystal consist of a layer of some sort of material of a different composition, strongly absorbing light. Upon making the crystal thinner, the thickness of non-absorbent substance is decreased, while the thickness of the absorbing layer remains unchanged. As the coefficient of absorption is calculated from measurements of the thickness of the crystal, the impression is gained that it increases almost inversely to the thickness. As a visible model of this absorption, we may use the absorption of a plate of glass which has been colored on both sides with paint. As a decrease in the thickness of the glass in not expressed in the absorption of the layers of paint, but in the calculation of the coefficient of absorption for unit thickness, the impression will be obtained that the coefficient of absorption increases as the thickness of the glass decreases.

All these facts enable us to arrive at the conclusion that herapathite crystals

are of such a structure that the chief portion of the crystal, a polyiodide with the cation (4 Quin., $3H_2SO_4$, $2H^+$) and the anion I_3^-, contains adsorbed molecular iodine. The relation between color of the crystal and the amount of iodine added indicates that here there is adsorption in many layers, and that its mechanism is similar to the mechanism suggested by deBure, i.e., it is due to the oriented electric polarization of the adsorbed iodine molecules.

In fact, we have said above that during the solution of the iodine in polar solvents, the region of absorption of the iodine is shifted in the direction of short waves all the more strongly the greater the polarity of the solvent. This phenomenon is apparently to be explained by the polarization of molecules of iodine solvated with molecules of the solvent. The molecules of iodine adsorbed on the surfaces of the polyiodide of quinine sulfate will be polarized by the anions, I_3^-, and their region of absorption will be shifted in the direction of short wave length. These oriented dipoles of the first layer to be adsorbed will in their turn orient the dipoles of the molecules of iodine adjacent to them, and in consequence there will form a second layer of adsorbed iodine molecules. As the polarization of the molecules of iodine in the second layer is weaker than in the first, the shift of their absorption spectrum will also be weaker. The absorption spectrum of the third layer will be shifted to a still smaller degree. Thus, the more iodine is adsorbed on the surface of the crystal, the more will its region of absorption be broadened in the direction of long waves, approximating the long-wave boundary in the region of absorption of molecular iodine in vapor or in a non-polar solvent. This shift of the region of absorption is actually observed.

4 Quin., $3H_2SO_4$, 2HI, $2I_2$ has an absorption spectrum characteristic of the I_3^- ion, i.e., it absorbs in the near ultraviolet part of the spectrum, and has the long-wave boundary of its region of absorption in the extreme violet and part of the blue rays. Crystals of such a polyiodide have a yellow color. The first layer of iodine molecules adsorbed has an absorption spectrum shifted in the direction of short waves, and therefore transmits red and orange rays, as a result of which the herapathite crystals with a low iodine content are colored red. In addition, the monomolecular layer has a comparatively weak general absorption, a fact which also explains the general course of the transmission curve of the red crystals of herapathite (cf. Fig. 2). With an increase in the amount of adsorbed iodine, the absorption of the iodine layer is shifted more and more in the direction of long waves, so that as a result the crystals are colored purple, lilac, and blue, in the order indicated previously. As the thickness of the adsorbed layer of iodine is increased more and more, its general absorption also increases, leading to the formation of the maximum of transmission in the region about 500 mμ as noted above. This, in combination with the shift of the region of absorption toward the boundary of the visible spectrum from the long-wave direction, also lends the crystals a blue color.

Completely analogous are the various phenomena observed in the films of polyvinyl alcohol during their impregnation with iodine, with the difference, however, that here the role of the cation is played by the micelle of polyvinyl alcohol (Fig. 4).

The essential role in the formation of the optical properties of the polyiodides considered is played by the orientation of the adsorbed molecules of iodine.

The very fact of the existence of pleochroism indicates the presence of orientation. In fact, pleochroism can arise only as a result of the existence of anisotropism either in the molecules themselves or in their arrangement. But for the anisotropism of the molecules to be detected, it is necessary that the molecules be arranged at random.

The experiments of L.P.Churaev and the hypothesis expressed previously with regard to the structure of the polyiodides under consideration lead to the conclusion that the pleochroism of these compounds is related to an overwhelming degree to the adsorbed layer of iodine.

Thin layers of iodine (of the order of 1μ), as Bovis has shown, actually show considerable pleochroism. Molecules of iodine adsorbed in many layers, under conditions in which they have a uniform orientation form around crystals or micelles of the lower polyiodides a kind of thin film of crystalline iodine. This fundamentally also determines the pleochroism of polyiodides of this type.

The pleochroism of polyiodides can arise only in case the electrically polarized molecules of iodine prove to be oriented in a single direction, and that, moreover, so that the dipole axis is parallel to the direction of the light vector. This orientation may arise in the adsorbed iodine on the surface of the crystals or colloid micelles.

The addition of molecules of iodine to the I_3^- ion by forces of "secondary" polarization cannot be considered as the formation of a chemical compound in the sense of the formation of new molecules, with the maintenance of stoichiometric relations between the elements forming them. To the contrary, all the facts given in the literature with regard to the composition and behavior of polyiodides under different conditions, and our own observations as well, rather indicate the indefiniteness of the composition of the higher polyiodides.

Everything said above leads to the structural scheme of "adsorbing polyiodides" represented in Fig. 5. By this term we shall refer to herapathite, starch-iodine, and the other similar compounds of iodine having the optical properties described above.

The basis of the compound is the anisotropic network of the crystal formed by a complicated cation of great volume and the anion I_3^-, possibly of deformed structure, forming positively charged and oriented micelles, which play the role of cations, and the anions I_3^-. Because of the large volume of the cation, the distance between the ions may be considered large, in each case surpassing the dimensions of a molecule of iodine.

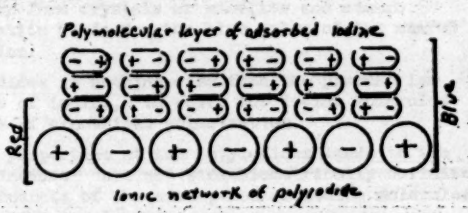


Fig. 5. Scheme for the formation of "adsorbing polyiodides" and the structure of the polymolecular adsorbed layers of iodine on the surface of the crystals of oriented structure.

The scheme of vanArkel and deBure supposes that the dipole axis of the adsorbed and oriented molecules of iodine is perpendicular to the adsorbing surface. With this arrangement of molecules, it is impossible, however, to expect the formation of pleochroism, as the electric pole of the molecules during this orientation will be symmetrical with respect to the direction of the electric vector of the light waves falling on the surface of the crystal. Even dichroism is possible only in the absence of such symmetry. Therefore, deBure's scheme must be modified in such a manner as to explain the pleochroism that occurs. This can be done in the following manner.

The positive pole of the dipole oriented by the I_3^- ion in the first molecules adsorbed is attracted to the I_3^- ion, the negative pole being attracted to the

cation (for example, 4 Quin., $3H_2SO_4$, $2H^+$) which is separated from the I_3^- anion by a distance equal to or somewhat greater than the diameter of an iodine molecule. Thus, the dipole axis is oriented in the direction of the powerful lines of the interionic poles on the surface of the crystal and can even be parallel to the adsorbing surface.

The same arrangement of the dipole axes of the second adsorbed layer of iodine molecules, however, differs in that the poles of these are arranged opposite the first layer, and the dipole moments of the latter are less.

Thus, this scheme explains not only the pleochroism, but also the change in the absorption spectra of the "adsorbing polyiodides" as the amount of iodine added is increased.

To this we must add that the pleochroism of these compounds may be found only in case the elementary crystals or micelles of the polyiodides are spatially oriented. This orientation may be produced either mechanically by the stretching of films, by streaming sols or suspensions, by orienting electric poles, or by any other methods.

SUMMARY

1. An investigation of the chemical reactions of iodine with polymolecular complexes of quinine and with polyvinyl alcohol sols, as well as a comparison of the results obtained with the data on the iodine-starch reaction, leads to the conclusion that in all these cases there is the formation of "adsorbing polyiodides".

2. An investigation of the absorption spectra and of the pleochroism of the compounds shows that the color of the polyiodide is produced by the displacement of the absorption spectra of the I_3^- anion, which enters into the composition of the compounds: the latter form crystals or micelles and adsorb molecular iodine. The same explanation holds for the blue color of the starch observed in the iodine-starch reaction.

The pleochroism of the polyiodides is nothing else than the pleochorism of the polymolecular adsorbed layers of iodine, in which the iodine molecules are oriented and in different stages of electrical polarization.

3. An analysis of the optical properties of the polyiodides leads to the conclusion that the "adsorbing polyiodides" are not stoichiometrically definite compounds, but may be regarded as products of the adsorption of iodine molecules upon the hetero-polarized compounds with the I_3^- anion.

4. A structural scheme is suggested for this type of polyiodide, in order to explain the optical properties.

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A PHYSICO-CHEMICAL INVESTIGATION OF THE SYSTEM

NH_4Cl - Al_2Br_6 - NITROBENZENE

(Electrical conductivity, viscosity and specific gravity)

I. S. Bigich

Zhitomir Agricultural Institute

In the works of many investigators who have studied the relationship between electrical conductivity and viscosity, it is shown that when a correction is made for the viscosity, the curves for molecular electrical conductivity in the region of concentrated solutions take on an anomalous character [1,2,3].

E.Ya.Gorenbein [4] has developed a theory of current-conducting complexes, and on the basis of the relationship between electrical conductivity and viscosity has arrived at the conclusion that a maximum in the curve for molecular electrical conductivity is the result of a sharp increase in the viscosity of the solution. Upon introducing a correction for the viscosity, the maximum in the $M_1 - \varphi$ curve disappears.

E.Ya.Gorenbein explains the anomalous course of the curves by the disintegration of the structural group upon dilution. In solutions with a high dielectric constant, the corrected molecular conductivity decreases upon dilution, passes through a minimum, and then rises. Our investigations of molecular electrical conductivity, taking account of the viscosity of the complexes $NaCl \cdot Al_2Br_6$ [5], $NaBr \cdot Al_2Br_6$ [6], $KBr \cdot Al_2Br_6$ [7], $NH_4Br \cdot Al_2Br_6$ [7] in nitrobenzene, showed that the corrected molecular electrical conductivity, with an increase in the concentration of electrolyte, independently of the nature of the complex, for concentrated solutions took on an "anomalous" character.

In order to follow the character of the curves of the corrected molecular electrical conductivity with other electrolytes, we investigated the electrical conductivity, viscosity, and specific gravity of the system $NH_4Cl \cdot Al_2Br_6$ in nitrobenzene, in relation to concentration and temperature.

The measurements of electrical conductivity, viscosity and specific gravity, and the preparation of the solutions of the complex $NH_4Cl \cdot Al_2Br_6$ to be investigated were the same as described in a previous communication [5].

Solutions of the necessary concentration in nitrobenzene were prepared so that simultaneous measurements might be made of electrical conductivity, viscosity, and specific gravity.

Solution of the complex $NH_4Cl \cdot Al_2Br_6$ in nitrobenzene produces a colored solution, whose intensity varies with the amount of complex present. The solution first has a straw-yellow color, and then as the concentration is raised, changes into a cherry red, i.e., solutions with a high content of the complex have a deeper color than solutions which have a low concentration.

An Arrhenius vessel, a viscosimeter, and a pyknometer containing the solution

TABLE 1

$NH_4Cl \cdot Al_2Br_6$ in Nitrobenzene at 20°

% of complex	$\varkappa \cdot 10^3$	$\varkappa \cdot 10^2$	φ	M	M'
5.09	2.435	0.2748	9300.7	22.6472	24.97
11.02	4.321	0.5871	4157.6	17.9650	24.408
15.96	5.338	0.8685	2779.1	14.8348	24.137
20.30	5.637	1.0819	2126.9	11.9888	23.010
25.33	5.827	1.4053	1650.4	9.6169	23.194
30.40	5.603	1.9246	1265.8	7.0924	24.362
34.32	5.139	2.0914	1146.8	5.8934	23.984
39.44	4.423	2.5052	963.21	4.2602	24.130
43.44	3.741	2.8552	849.8	3.1791	24.264
48.63	2.787	3.4720	730.2	2.0353	25.356
54.05	1.195	4.3038	630.0	1.2065	27.110

TABLE 2

$NH_4Cl \cdot Al_2Br_6$ in Nitrobenzene at 30°

% of complex	$\varkappa \cdot 10^3$	$\varkappa' \cdot 10^2$	φ	M	M'
5.09	2.828	0.3046	9374.0	26.5097	28.551
11.02	4.964	0.6516	4189.7	20.7977	27.301
15.96	6.365	1.2451	2801.1	17.8290	27.085
20.30	6.874	1.2032	2143.4	14.7337	25.790
25.33	7.159	1.5373	1663.2	11.9068	25.568
30.40	6.950	2.0419	1275.8	8.6678	24.801
34.32	6.504	2.2245	1155.9	7.5179	25.077
39.44	5.800	2.6142	970.6	5.6225	25.374
43.44	5.257	3.0046	856.6	4.5031	25.738
48.63	4.208	3.6208	736.0	3.0971	26.649
54.05	3.144	4.3943	635.0	1.9964	27.903

TABLE 3

$NH_4Cl \cdot Al_2Br_6$ in Nitrobenzene at 40°

% of complex	$\varkappa \cdot 10^3$	$\varkappa' \cdot 10^2$	φ	M	M'
5.09	3.181	0.3270	9447.8	30.0534	31.393
11.02	5.641	0.6944	4223.5	23.8248	29.329
15.96	7.318	1.0235	2830.0	20.3591	29.401
20.30	7.868	1.2612	2160.2	16.9965	27.244
25.33	8.368	1.6098	1675.7	14.0222	26.975
30.40	8.450	2.1629	1285.5	10.8625	26.620
34.32	8.144	2.3524	1164.9	9.4886	26.377
39.44	7.557	2.7830	977.0	7.3900	27.215
43.44	6.925	3.1441	862.8	5.9749	27.128
48.63	5.816	3.6729	741.4	4.3120	27.231
54.05	4.610	4.4833	630.1	2.9485	28.675

TABLE 4

$NH_4Cl \cdot Al_2Br_6$ in Nitrobenzene at 50°

% of complex	$\kappa \cdot 10^3$	$\kappa' \cdot 10^2$	φ	M	M'
5.09	3.597	0.3572	9525.1	34.2618	34.029
11.02	6.444	0.7562	4256.3	27.4276	32.185
15.96	8.398	1.0972	2844.5	23.8767	31.920
20.30	9.328	1.3991	2176.9	20.3061	30.457
25.33	9.787	1.7259	1688.2	16.5240	29.136
30.40	9.970		1295.2	12.9130	28.301
34.32	9.703	2.4912	1173.6	11.3991	27.441
39.44	9.208	2.9191	985.2	9.0717	28.758
43.44	8.554	3.2576	865.2	7.4351	28.314
48.63	7.500	3.9049	746.8	5.6011	29.136
54.05	6.291	4.6834	644.2	4.0527	30.174

under investigation were placed in a water thermostat. During the time of measurement, the temperature of the thermostat varied within the limits of 0.1°.

An electrochemical investigation of the solutions of the ternary system consisting of $NH_4Cl - AlBr_3 - C_6H_5NO_2$ has shown that the specific electrical conductivity [8] of the binary system aluminum bromide – nitrobenzene increases linearly with an increase in the concentration of NH_4Cl and in absolute value is several times greater than the electrical conductivity of a nitrobenzene solution of aluminum bromide.

The results of measurement of the specific electrical conductivity of the system we investigated, $NH_4Cl \cdot Al_2Br_6$ – nitrobenzene, are listed in Tables 1 to 4 and shown graphically in Fig. 1.

The curves of Fig. 1 characterize the relationship of the specific electrical conductivity to the temperature and the concentration of electrolyte.

As can be seen from Fig. 1, the value of the specific electrical conductivity of this system, as of the preceding system studied by us, increases with an increase in the concentration of the complex, passes through a maximum, and then gradually falls.

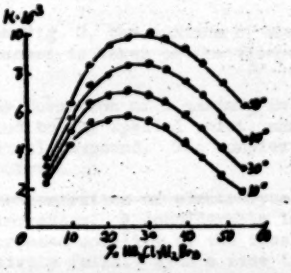

Fig. 1. Specific electrical conductivity of the complex $NH_4Cl \cdot Al_2Br_6$ in nitrobenzene.

The maximum on the curves corresponds to from 25 to 30% of complex.

With a rise in the temperature, the value of the specific electrical conductivity increases linearly for high concentrations and changes with the dilution. With a rise in temperature, the maximum shifts in the direction of higher concentrations of the complex.

We calculated the specific electrical conductivity corrected for viscosity for those concentrations of the solution for which we had measured the specific electrical conductivity. In our calculations, we used the formula indicated for the system $NaCl \cdot Al_2Br_6 - C_6H_5NO_2$, [5].

In Tables 1 to 4 are shown the values of specific electrical conduc-

tivity corrected for viscosity. The curves of Fig. 2 express the relationship between specific electrical conductivity, corrected for viscosity, and the concentration of the complex and the temperature.

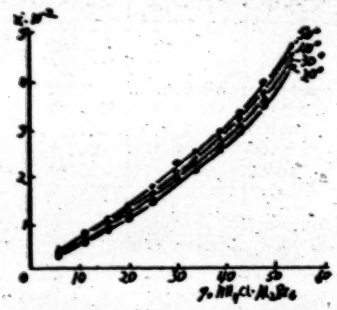

Fig. 2. Specific electrical conductivity corrected for viscosity of the complex $NH_4Cl \cdot Al_2Br_6$ in nitrobenzene.

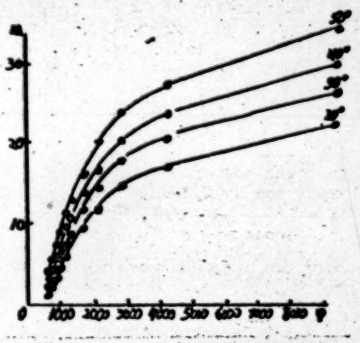

Fig. 3. Molecular electrical conductivity of the complex $NH_4Cl \cdot Al_2Br_6$ in nitrobenzene.

As can be seen from Tables 1 to 4 and from Fig. 2, the maximum of specific electrical conductivity curves disappears when account is taken of the viscosity and these curves are convex toward the abscissas.

In our previous work [5] we noted that the formation of a maximum in the specific electrical conductivity did not correspond to any special point, and did not indicate the formation of a definite chemical compound, The complex $NH_4Cl \cdot Al_2Br_6$ may be classified as a binary electrolyte.

From the tables it is clear that as the concentration of electrolyte increases, the viscosity of the solution likewise increases. A considerable increase in the viscosity of the solution results in a decreased mobility of the ions, as a result of which the specific electrical conductivity falls. With a rise in the temperature, the specific electrical conductivity, when account is taken of the viscosity, rises.

The molecular electrical conductivity was calculated for an electrolyte with the composition $NH_4Cl \cdot Al_2Br_6$. The results obtained for the molecular electrical conductivity are listed in Tables 1 to 4 and shown graphically in Fig. 3.

The curves of Fig. 3 express the relationship $M = \underline{f}(\varphi)$ for the system $NH_4Cl \cdot Al_2Br_6 - C_6H_5NO_2$.

As can be seen from Tables 1 to 4 and from Fig. 3, the value of the molecular electrical conductivity increases with the dilution, and in their general shape the curves recall the curves of molecular electrical conductivity of systems previously studied by us, consisting of complex compounds of aluminum bromide in nitrobenzene [5-7].

The molecular electrical conductivity of the complex $NH_4Cl \cdot Al_2Br_6$ in nitrobenzene is somewhat greater than the molecular electrical conductivity of aluminum bromide in nitrobenzene [9].

Tables 1 to 4 give the values of the molecular electrical conductivity corrected for viscosity. The curves of Fig. 4 express the relationship $M' = f(q)$.

As can be seen from Tables 1 to 4 and from Fig. 4, with an increase in the concentration of electrolyte, the corrected molecular conductivity first decreases, passes through a minimum, and then gradually increases. This course of the curves confirms the hypothesis expressed by E.Ya.Gorenbein [4], that every soluble substance attempts to attain the same sort of condition as if it were in a molten condition, for the highest value of the corrected molecular electrical conductivity must correspond to the corrected molecular electrical conductivity of the individual electrolyte in the molten condition.

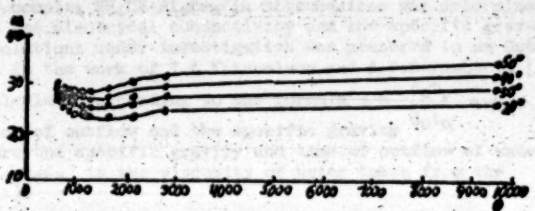

Fig. 4. Corrected molecular electrical conductivity of the complex $NH_4Cl \cdot Al_2Br_6$ in nitrobenzene.

Specific Gravity

The specific gravity of the complex $NH_4Cl \cdot Al_2Br_6$ in nitrobenzene was investigated under the same conditions as the electrical conductivity. The measurements of the specific gravity were carried out in a pyknometer with a ground glass stopper, with a narrow neck graduated to 0.01 cm^3.

The values of the specific gravity obtained are listed in Table 5 and shown graphically in Fig. 5, where weight percentages of the complex are laid off along the axis of abscissas and values of the specific gravity along the axis of ordinates.

TABLE 5

Specific Gravity of Solutions of $NH_4Cl \cdot Al_2Br_6$ in nitrobenzene.

% of complex	20°	30°	40°	50°
5.09	1.2387	1.2290	1.2194	1.2095
11.02	1.2811	1.2713	1.2611	1.2514
15.96	1.3231	1.3127	1.3030	1.2927
20.30	1.3594	1.3490	1.3385	1.3282
25.33	1.4041	1.3933	1.3829	1.3727
30.40	1.4523	1.4410	1.4300	1.4194
34.32	1.4912	1.4795	1.4681	1.4572
39.44	1.5447	1.5329	1.5215	1.5102
43.44	1.5898	1.5773	1.5659	1.5543
48.63	1.6527	1.6398	1.6479	1.6161
54.05	1.7235	1.7100	1.6976	1.6856

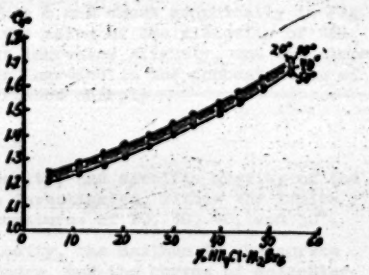

Fig. 5. Specific gravity of the complex $NH_4Cl \cdot Al_2Br_6$ in nitrobenzene.

As can be seen from Table 5 and Fig. 5, the specific gravity curves are convex to the axis of abscissas, and the specific gravity increases with an increase in concentration.

A rise in temperature leads to a decrease in specific gravity, which changes linearly.

Viscosity

The viscosity of the complex $NH_4Cl \cdot Al_2Br_6$ in nitrobenzene was determined under the same conditions as the electrical conductivity and the specific gravity. The viscosity of the solutions under investigation was measured in an Ostwald viscosimeter, described in the work of I.L.Katsnelson and A.V.Bernshtein [10].

The viscosity was calculated according to the formula $\eta = \frac{d_p t_p}{d_o t_o} \eta_{abs.}$, where t and d are the duration of outflow and the specific gravity of the solution, d_o and t_o are the specific gravity and time of outflow of water at the same temperature, and $\eta_{abs.}$ is the viscosity of water taken from the Landolt—Börnstein tables [11].

TABLE 6

Viscosity of Solutions of $NH_4Cl \cdot Al_2Br_6$ in Nitrobenzene

% of complex	20°	30°	40°	50°
5.09	2.2280	1.8094	1.4805	1.2415
11.02	2.7445	2.2053	1.7727	1.4668
15.96	3.2866	2.5522	2.0359	1.6711
20.30	3.8770	2.9407	2.3082	1.8749
25.33	4.8718	3.6076	2.7702	2.2043
30.40	6.9380	4.8669	3.6519	2.8379
34.32	8.2208	5.6060	4.0031	3.0100
39.44	11.4415	7.5772	5.3032	3.9626
43.44	15.4171	9.6022	6.5381	4.7603
48.63	25.1655	14.4556	9.0940	6.5083
54.05	45.3902	23.4810	14.0045	9.3058

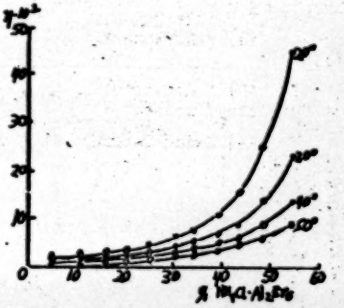

Fig. 6. Viscosity of the complex $NH_4Cl \cdot Al_2Br_6$ in nitrobenzene

The results obtained are given in Table 6 and shown graphically in Fig. 6. As can be seen from Table 6 and Fig. 6, the value of the viscosity of the solution from 5.09 to 30.40% of complex first increases slightly, and the slope of the curves is not high, but with a further increase in the concentration of the complex, the steepness of the curves increases sharply.

SUMMARY

1. The electrical conductivity, viscosity, and specific gravity of the complex $NH_4 \cdot Al_2Br_6$ in nitrobenzene have been investigated, within the limits of concentration from 5.09 to 54.5%, at temperatures of 20, 30, 40, and 50°.

2. When account is taken of the viscosity, the maximum in the curves for specific electrical conductivity disappears, and the curves of molecular electrical conductivity in the region of high concentrations take on an anomalous character. This course of the curves confirms the hypothesis expressed by E.Ya.Gorenbein about the nature of concentrated solutions.

3. The specific and molecular electrical conductivity increase as the temperature rises, while the viscosity falls.

4. The curves for specific gravity are convex toward the axis of abscissas.

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THE QUESTION OF THE THEORY OF THE DISTRIBUTION OF IONS BETWEEN SOLID PHASES AND A LIQUID SOLUTION

N. V. Shishkin and E. A. Krogius

Saratov State University

The laws of the distribution of ions between solid phases and a liquid solution have been used by us in considering the nature of several solid phases formed in heterogeneous salt systems. Among a number of other data, we utilized them in investigating one of the most interesting cases of isomorphism, in order to shed light on the structure of a number of representatives of a group of unstable and difficultly soluble complex compounds: the isomorphism in a number of oxonium ions on the one hand and of ammonium and alkali metal group ions on the other.

As materials to be studied, we used a group of ferric oxide sulfates, crystallizing in the neutral and acid regions of the ternary system $H_2O - SO_3 - Fe_2O_3$. These are typical representatives of this little-studied group of complex compounds. Data obtained in our laboratory during an investigation of the equilibrium in the quaternary iron sulfate system $H_2O - SO_3 - Fe_2O_3 - (NH_4)_2O$ lead us to the conclusion that all these sulfates are based on one and the same complex anion $Fe(SO_4)_2'$, which also enters into the composition of the anhydrous analogs of the iron alums.

In this study, the acid trihydrated sulfate $Fe_2O_3 \cdot 4SO_3 \cdot 3H_2O$ was of special interest. On the basis of considerable data, this had to be considered as a product formed from the anhydrous alum as a result of the isomorphous substitution of the ammonium or alkaline metal group ion by a hydroxyl ion.

If these compounds are representative, then in equilibrium systems containing anhydrous iron ammonium alum as the solid phase, there is a single solid phase in equilibrium with the solution – an isomorphous mixture of two salts containing the same anion.

In cases where the anhydrous alum and one of the other sulfates noted above are present at the same time, there is an equilibrium between the solution and the two salts having a common anion, without the formation of mixed crystals. Each of these two cases of equilibrium must be considered as corresponding to definite laws for the distribution of the cations between the solid phases and the liquid solution.

The derivation of these laws, and a short presentation of the data obtained in their investigation for the purpose mentioned above, constitute the content of the present article.

The questions involved in the theory of the distribution of ions between the phases of a heterogeneous system have attracted numerous investigators, who have studied the exchange of ions in the aluminosilicates. After considerable experimental and theoretical work, these investigators have gradually explained

the laws of this exchange, embodying their final formulation in the equation given by Vanselow [1], and in more general and more rigorous form by B.P.Nikolsky [2];

$$\frac{a_{l_1}^{\frac{1}{z_1}}}{a_{l_2}^{\frac{1}{z_2}}} = K \frac{a_{s_1}^{\frac{1}{z_1}}}{a_{s_2}^{\frac{1}{z_2}}}.$$

Here a_{l_1} and a_{l_2} represent the activities of the primary and secondary cations in the liquid phase, a_{s_1} and a_{s_2} the activities of these components in the solid phase, and z_1 and z_2 the valences of the cations.

This equation was deduced for a special case, when the solid phase, regarded as a solid solution of two salts with an identical anion, was insoluble, the anion not being contained in the liquid phase and not taking part in the exchange [2]. Therefore, this equation could not be directly utilized for our purpose. It was necessary to revise the theory by applying it to those conditions which held for the system under investigation, where the solid phases were very soluble, and the anion which formed part of these phases existed also in the liquid phase and took part in this exchange. In this way, as a result of the conclusions of N.V.Shishkin given below, there was obtained an equation which formulated the law for the distribution of the cations for two of the cases indicated above.

To obtain these conclusions it is assumed that the temperature and volume or the temperature and pressure are maintained constant and that the mobile molecular groups, both in the liquid solution and in the solid phases,* are ions.

As the temperature and volume or the temperature and pressure are constant, these systems will be in stable equilibrium if during all possible infinitely small changes the free energy at constant volume or the free energy at constant pressure remains unchanged, that is, if $dF = 0$ or $d\phi = 0$. And as under the conditions indicated above, in the systems being considered the only possible changes are the transfer from one phase to the other of the algebraic sums of the ions (the sums of equivalent amounts of those of different sign or the differences between those of the same sign) then the condition for equilibrium leads to the requirement that the algebraic sum of the chemical potentials of the ions leaving one phase be equal to the algebraic sum of the chemical potentials of these ions in that phase which these ions are entering. In other words, that the algebraic sums of the chemical potentials of the ions free to move from one phase to another be the same in both phases.

I. Two Soluble Salts of Constant Composition with Identical Anion, Not Forming an Isomorphous Mixture With Each Other, Plus Solution

In this case, the passage from solid phases to liquid and vice versa in significant quantities can only take place for the sums of the equivalent amounts of ions of different signs. In respect to this possible passage, the system must also be in equilibrium. For this it is necessary that the sum of the chemical potentials of the equivalent quantities of cations and anions of each salt in the solution be equal to the sums of the chemical potentials of these quantities of the ions in the solid phases, i.e., equal to constants:

$$\nu_{c_1}\mu_{c_1} + \nu_{a_1}\mu_a = \text{const.}_1; \quad a_{c_1}^{\nu_{c_1}} \cdot a_a^{\nu_{a_1}} = K_1,$$

$$\nu_{c_2}\mu_{c_2} + \nu_{a_2}\mu_a = \text{const.}_2; \quad a_{c_2}^{\nu_{c_2}} \cdot a_a^{\nu_{a_2}} = K_2.$$

* In the latter case we speak of potential mobility, which appears upon contact with the liquid solution.

In these equations, the symbols ν signify the numbers of ions in the chemical formulas of the electrolytes. The first index, placed below the symbols ν and μ, gives the sign of the ion (cation or anion), and the second index the number of the ion; K_1 and K_2 are constants.

Extracting from both sides of the first equation the ν_{a1}th root, and from both sides of the second equation the ν_{a2}th root, and substituting the first equation in the second, we obtain:

$$\frac{a_{c1}^{\frac{\nu_{c1}}{\nu_{a1}}}}{a_{c2}^{\frac{\nu_{c2}}{\nu_{a2}}}} = \text{const.}$$

As the ratio of the number of cations to the number of anions in the chemical formula of any electrolyte is inversely proportional to the ratio of the valences of these ions, we can write:

$$\frac{\nu_{c1}}{\nu_{a1}} = \frac{z_a}{z_{c1}}; \quad \frac{\nu_{c2}}{\nu_{a2}} = \frac{z_a}{z_{c2}},$$

where z_{c1} and z_{c2} are the valences of the cations of the first and second salts, and z_a is the valence of the anion, which is common to both.

Substituting in the previous equation for the ratio of the numbers of cations to the numbers of anions the ratio of the valences of these ions and extracting from both sides of the equation the z_a th root, we obtain:

$$(1) \quad \frac{a_{c1}^{\frac{1}{z_{c1}}}}{a_{c2}^{\frac{1}{z_{c2}}}} = \text{const.}$$

If the concentrations of all the components of the solution except one are relatively small, and change little, the activity coefficients of the ions in the liquid solution may be taken as approximately constant. We may also take as constant the percentage of solvent in the solution.

Under these conditions, Equation (1) leads to the equation:

$$(1a) \quad \frac{\underline{m}_{c1}^{\frac{1}{z_{c1}}}}{\underline{m}_{c2}^{\frac{1}{z_{c2}}}} = \text{const.}; \qquad \frac{g_{c1}^{\frac{1}{z_{c1}}}}{g_{c2}^{\frac{1}{z_{c2}}}} = \text{const.},$$

where $\underline{m}$ signifies molarity and g the weight percent of cations in the liquid solution.

If the percentage of one of the cations in the solution, for example the second cation, does not change or changes very little, the latter equation leads to the equation:

$$(1b) \qquad g_{c1} = \text{const.}$$

This constancy of the percentage of the first cation in the liquid solution, even during considerable relative changes of its content in the total composition of the system, must be examined more closely in the case where the valence of the

second cation is greater than the valence of the first, for example when $z_1 = 1$ and $z_2 = 3$. In this case, even if the content of the second cation in the solution did not remain completely constant, its cube root would be more nearly constant, and therefore, the percentage of the first cation would also remain constant.

These considerations lead to the following conclusions. If two salts of constant composition with an identical anion and cations of different valences are in equilibrium in a solution, then even if there are considerable relative changes in the total composition of the system with regard to the amount of univalent cation, the percentage of this cation in the liquid solution will remain approximately constant if its amount is small in comparison with the amounts of the other components in the system. The amounts of the latter in the total composition of the system will be unchanged or change very little.

II. Isomorphic Mixtures of Two Salts with an Identical Anion Plus Liquid Solution

If we may regard the isomorphous mixture as a solid solution, then this case represents a distribution of cations between two solutions, one of which is an isomorphous mixture.

Two cases are possible:

1) The solid phase is practically insoluble in the liquid solution and has a tendency to absorb cations from it, extracting from the solution an equivalent amount of cations of the other type.

2) The isomorphous mixture is soluble.

In the first case, the only change possible in the system is the transfer from one phase to the other of the difference in the equivalent amounts of the different cations. The equilibrium of the system must be an equilibrium with respect to this single change. An example of this type of equilibrium is the exchange of ions in aluminosilicates.

In the second case, two kinds of change are possible in the system. In addition to the transfer of the difference between the equivalents of ions with the same sign (cations) there can also take place in the system a transfer of the sum of equivalents of ions of different signs. The equilibrium of the system must be an equilibrium with respect to both these possible kinds of transfer.

However, it can be shown that the second possibility does not introduce any additional peculiarities into the law for the distribution of ions.

In both cases, we shall take the ions as mobile molecular groups in the liquid and solid solutions. For them we must also calculate the chemical potentials in order to obtain the laws of distribution.

Case 1. The single change possible in the system is the transfer of the difference between equivalents of the cation in common. The equilibrium condition will in this case be formulated by the equation:

$$z_2\mu_{1l} - z_1\mu_{2l} = z_2\mu_{1s} - z_1\mu_{2s},$$

from which we obtain Nikolsky's equation (cf. p. 1026).

Case 2. The isomorphous mixture of two salts with an identical anion is soluble in the liquid solution. In this case, as indicated above, two sorts of changes are possible in the system. The equilibrium condition with regard to the first of these changes – the transfer of the difference in equivalents of the cations – is formulated exactly as in the given equation. The condition for

equilibrium with regard to the second of the possible changes – the transfer of the sums of equivalents of ions of different sign – is formulated by the equations:

$$\nu_{c1}\mu_{c1l} + \nu_{a1}\mu_{al} = \nu_{c1}\mu_{c1s} + \nu_{a1}\mu_{as},$$

$$\nu_{c2}\mu_{c2l} + \nu_{a2}\mu_{al} = \nu_{c2}\mu_{c2s} + \nu_{a2}\mu_{as}.$$

These equations lead to the equations:

$$\underline{a}_{c1l}^{\nu_{c1}} \cdot \underline{a}_{al}^{\nu_{a1}} = K_1 \cdot \underline{a}_{c1s}^{\nu_{c1}} \cdot \underline{a}_{as}^{\nu_{a1}},$$

$$\underline{a}_{c2l}^{\nu_{c2}} \cdot \underline{a}_{al}^{\nu_{a2}} = K_2 \cdot \underline{a}_{c2s}^{\nu_{c2}} \cdot \underline{a}_{as}^{\nu_{a2}}.$$

In these equations, as in the previous ones, the symbols ν signify the numbers of ions in the chemical formulas of the electrolytes; μ_{c1l} and $\underline{a}_{c1l}$ are the chemical potentials and activity of the cation of the first salt in liquid solution; μ_{c1s} and $\underline{a}_{c1s}$ the chemical potential and activity of the cation of this salt in the solid solution. The chemical potential and activity of the anion are symbolized in the same way, but without the index corresponding to the number of the salt; K_1 and K_2 are constants.

Raising both sides of the first of these equations to the power $\frac{1}{\nu_{a1}}$, and both sides of the second to the power $\frac{1}{\nu_{a2}}$, and substituting one of these equations in the other, we obtain:

$$\frac{\underline{a}_{c1l}^{\frac{\nu_{c1}}{\nu_{a1}}}}{\underline{a}_{c2l}^{\frac{\nu_{c2}}{\nu_{a2}}}} = K \frac{\underline{a}_{c1s}^{\frac{\nu_{c1}}{\nu_{a1}}}}{\underline{a}_{c2s}^{\frac{\nu_{c2}}{\nu_{a2}}}},$$

where K is the distribution constant. But as has been said previously, the ratio of the numbers of cations and of anions in the chemical formula of the electrolyte is inversely proportional to the ratio of their valences, and therefore this equation can be put in the form:

$$\frac{\underline{a}_{c1l}^{\frac{1}{z_1}}}{\underline{a}_{c2l}^{\frac{1}{z_2}}} = K \frac{\underline{a}_{c1s}^{\frac{1}{z_1}}}{\underline{a}_{c2s}^{\frac{1}{z_2}}}. \qquad (2)$$

Thus, Nikolsky's equation remains valid for the second case also, when the solid phase is soluble in the liquid solution; the anion which composes part of the solid phase also exists in the liquid phase and takes part in the exchange.

If the activity coefficients of the cations in the solid phase do not change very considerably as a result of the substitution of one of the ions by an isomorphic ion with properties resembling its own, and if, in addition, under the conditions of the experiments we may assume that in the liquid phase the activity coefficients of these ions remain approximately constant, then the activity of the cation in the latter equation may be replaced by its molar fraction:

$$\frac{N_{1l}^{\frac{1}{z_1}}}{N_{2l}^{\frac{1}{z_2}}} = K \frac{N_{1s}^{\frac{1}{z_1}}}{N_{2s}^{\frac{1}{z_2}}} .$$

N_{1l}, N_{2l}, N_{1s}, and N_{2s} signify the molar fractions of the first and second cations in the liquid and solid solutions. If, as is true in the case of genuine mixed crystals, the valences of the cations which take part in the distribution are equal, the latter equation leads to the equation:

$$\frac{N_{1l}}{N_{2l}} = K \frac{N_{1s}}{N_{2s}} ,$$

and this to the equation:

$$(2a) \qquad \frac{m_{1l}}{m_{2l}} = K \frac{m_{1s}}{m_{2s}}$$

and

$$\frac{g_{1l}}{g_{2l}} = K \frac{g_{1s}}{g_{2s}} .$$

In these equations, m, with the corresponding index, signifies the molarity and g the weight percent of cations in the liquid (l) and solid (s) phases.

For the process of distribution in those cases where the percentage of the second cation in the liquid phase may be taken as constant, the latter equation gives:

$$(2b) \qquad g_{1l} = K \frac{g_{1s}}{g_{2s}} .$$

It is in this latter form that the equation for distribution was utilized by us. The constancy of the distribution coefficient, K, calculated according to Equation (2b), serves to indicate that the cations which take part in the distribution substitute for each other isomorphously in the solid phase, while their activity coefficients change little.

In a study of the distribution of very small quantities of any salt (microcomponent) between crystals and a saturated solution of a second salt (macrocomponent) isomorphous with the first salt and having an anion in common with it, Equation (2a) leads to the equation:

$$g_{1l} = K \cdot \frac{g_{1s}}{g_{2s}} ,$$

i.e., the percentages of microcomponent in the liquid and solid phases are proportional.

EXPERIMENTAL

Tables 1, 2, and 3 give the experimental data obtained by us in an investigation of the distribution of cations in the quaternary equilibrium system $H_2O - SO_3 - Fe_2O_3 - (NH_4)_2O$ at a temperature of 100° in the crystallization ranges of neutral hexahydrates (Table 1), acid nonahydrates (Table 2), and acid trihydrates (Table 3) of iron sulfates, in the presence of anhydrous iron ammonium alum.

The experiments were carried out in such fashion that in the ternary system

TABLE 1

Equilibrium in the Range of Crystallization of the Neutral Hexahydrate of Iron Sulfate

In equilibrium with the solution are the neutral hexahydrated sulfate $Fe_2O_3 \cdot 3SO_3 \cdot 6H_2O$ and anhydrous iron ammonium alum $NH_4[Fe(SO_4)_2]$

No.	Amt. of $(NH_4)_2SO_4$ added to system	Original composition of system: 20 g $Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$, 10 cm^3 H_2O, 1 cm^3 H_2SO_4 (concentrated)						Precipitate under microscope
		Composition of liquid phase			Total composition of bottom phases (precipitates)			
		NH_4	Fe	SO_4	NH_4	Fe	SO_4	
1	0.01	0.066	6.46	39.31	0.17	22.77	58.68	Needles
2	0.01	0.063	6.80	40.73	0.20	23.00	61.22	Needles
3	0.05	0.072	7.41	38.28	0.22	20.49	59.40	Needles
4	0.1	0.086	–	–	0.28	22.65	59.64	Needles and few small hexagons
5	0.2	0.088	7.55	38.04	0.98	21.30	60.24	Same
6	0.5	0.089	7.59	38.38	2.8	21.72	65.76	Needles, hexagons
7	0.7	0.09	7.69	36.96	5.2	20.82	69.12	Same
8	1.0	0.084	7.65	35.18	6.38	20.76	71.36	Hexagons
9	1.0	0.073	–	–	6.76	21.02	72.0	Same
10	6	3.03	–	34.44	6.75	19.58	72.36	Fine granules

$H_2O - SO_3 - Fe_2O_3$ in the ranges of crystallization of one of the sulfates indicated above, small, gradually increasing amounts of ammonium sulfate were introduced. During this process, anhydrous iron ammonium alum was formed, in equilibrium with the liquid solution, along with the sulfates under investigation. The quantity of ammonium ion introduced into the system, even though its relative amount in the system changed considerably, remained small in comparison with the quantities of the other components of the system. These quantities either did not change or changed very little.

Under these conditions, the composition of the liquid solutions with regard to the components which were in large amount remained almost unchanged, and therefore the activity coefficients of the ions in solution could be considered as approximately constant, at least to the first rough approximation.

The systems were maintained in thermostats at a temperature of 100° for from 7 to 22 days. The experiments listed in Tables 1 and 3 were carried out in sealed glass ampoules which were revolved in air thermostats. The experiments of Table 2 were carried out in the usual small vessels for the study of equilibrium. In these latter experiments, a small amount of water evaporated. As a result of this, the total composition of the systems at the end of the experiments appeared changed in comparison with the original composition. The amount of water in the systems was decreased and corresponding to this, the percentages of the other components were increased.

All the analyses of the solid phases were carried out directly. The larger amounts of NH_4 in the solid and liquid phases were determined by distillation and titration with HCl, the smaller colorimetrically, with the aid of a photoelectric cell. The percentages of oxonium ions in the precipitate in Table 3 were calculated from the amount of ammonium in this precipitate. This could easily be done if account was taken of the fact that the precipitate was either a mixture or a solid solution of anhydrous iron ammonium alum and the trihydrate of iron sulfate.

When the number of ammonium ions introduced into the system is insufficient for complete conversion of the hexahydrated sulfate into anhydrous alum, both the anhydrous alum and the neutral hexahydrated sulfate will be in equilibrium with the solution. These salts do not form mixed crystals. When the precipitate is investigated under the microscope, its lack of uniformity is clearly seen: there are regular hexagonal plates of the anhydrous alum and needles of the hexahydrated sulfate.

Corresponding to the structural formulas proposed for the compounds:

$$NH_4[Fe(SO_4)_2] \quad \text{and} \quad [Fe(H_2O)_{12}][Fe(SO_4)_2]_3,$$

in this case there is an equilibrium between the solution and two salts with a common anion which do not form an isomorphous mixture.

The distribution of cations in this case must follow Equation (1).

In accordance with the data of Table 1, the percentage of iron in solution changes little when the amount of ammonium sulfate added to the system is changed. The iron in the solution is in the form of complex anions and hydrated iron ions. As the solubility of the anhydrous alum is small, we may consider that the relative stability of the iron content in the solution indicates that the percentage of iron cations in the solution changes little as the amount of ammonium sulfate added to the system is changed.

All the more can the cube root of this amount be considered constant. Under these conditions, the percentage of NH_4 in solution, in accordance with Equation (1b) must also remain constant; within the limits of experimental error and the lack of constancy of the activity coefficients, this fact is also confirmed by the data of Table 1.

The percentage of ammonium ions in the solution remains almost constant up to the point of complete transformation of the hexahydrated iron sulfate into anhydrous iron ammonium alum. After the point of complete conversion of the iron sulfate into anhydrous alum is reached, and there is a single solid phase in equilibrium with the solution, that of the anhydrous alum, then, with an increase in the amount of ammonium sulfate in the system there is a sharp increase in the amount of NH_4 in solution. In the solid phase, the amount of ammonium now remains constant (Experiment 10).

The acid nonahydrated sulfate, like the preceding salt, has no tendency to form mixed crystals with the anhydrous alum. In accordance with the structural formulas proposed for the compounds:

$$NH_4[FE(SO_4)_2] \quad \text{and} \quad [OH_3 \cdot 3H_2O][Fe(SO_4)_2],$$

the complex anion $Fe(SO_4)_2'$ in the anhydrous alum is united with the ammonium ion, and in the nonahydrated sulfate with the oxonium ion, the latter itself joined to three molecules of water. These cations differ considerably in their dimensions and in their nature, and therefore can hardly be expected to show a tendency to substitute isomorphously for each other in their compounds. Actually, the crystalline forms of these compounds are completely different, and so long as the amounts of ammonium ion added to the system are insufficient for complete conversion of the nonahydrated sulfate into anhydrous iron ammonium alum, the precipitate is nonhomogeneous. Upon carefully investigating it under the microscope, we could determine that it was a mixture of small hexagonal plates of anhydrous alum and typical rhombic crystals of the nonahydrated sulfate. In this case we find in equilibrium with the solution two salts with a common anion, which do not form isomorphous mixtures. We may therefore expect that the distribution of cations will follow Equation (1), and under the conditions of our experiments, Equation (1b), i.e., we may expect that the amount of ammonium ions in

TABLE 2

Equilibrium in the Range of Crystallization of the Acid Nonahydrated Sulfate

In equilibrium with the solution are the acid nonahydrated sulfate $Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$ and anhydrous iron ammonium alum $NH_4Fe(SO_4)_2$

No.	Amount of $(NH_4)_2SO_4$ added to system	Original composition of system: 10 g $Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$, 13 g H_2O, 17 g H_2SO_4 (concentrated)					
		Composition of liquid phase			Total composition of solid phases (precipitate)		
		NH_4	Fe	SO_4	NH_4	Fe	SO_4
		First group of experiments					
1	0.01	0.02	0.18	57.78	0.072	17.47	59.60
2	0.05	0.02	–	–	0.26	17.55	–
3	0.1	0.028	–	54.92	0.32	17.39	60.48
4	0.1	0.026	0.17	54.84	0.32	17.34	60.48
5	1	0.059	–	57.12	3.5	19.00	66.24
6	1	0.043	–	57.23	3.9	18.88	–
7	1	0.037	–	–	3.7	19.0	–
		Second group of experiments					
1	0.01	0.028	0.23	–	0.17		59.40
2	0.05	0.024	0.31	–	0.30		62.04
3	1	0.039	0.33	–	3.6		–
4	1.5	0.036	–	57.48	5.4		70.32
5	2	0.087	–	–	5.9		–
		Third group of experiments					
1	0.1	0.029	0.22	–	–	17.41	60.72
2	0.2	0.04	0.202	–	–	–	–
3	0.5	0.049	0.26	–	2.1	17.69	64.8
4	1	0.042	–	–	3.9	–	66.36
		Fourth group of experiments					
1	0.2	0.045	0.31	55.5	0.55	–	59.5
2	0.5	0.037	0.28	55.6	1.6	17.4	63.2
3	1.0	0.036	–	–	3.13	–	–
4	1.5	0.04	–	–	5	–	–

the solution will remain constant as the ammount of ammonium sulfate added to the system is changed, so long as crystals of the nonahydrated sulfate are present in the system along with crystals of anhydrous alum. In fact, in accordance with the data of Table 2, a change in the amount of ammonium sulfate added to the system produces little change in the percentage of ammonium in the solution. Thus, when the amount of ammonium sulfate is increased from 0.01 to 1 g, the percentage of ammonium in the solution increases in all from to 1.5 to 2.5 times its previous value.

The same degree of constancy as in the case of the hexahydrated sulfate is not observed here, and in this case there is undoubtedly a small increase in the percentage of ammonium ions. This cannot be explained away as experimental error and can hardly be explained by the lack of constancy of the activity coefficients of the ions. The more probable hypothesis is that in this range, as a result of the presence of a large number of hydrogen ions in the solution, there is already being shown the possibility of partial substitution of the ammonium ions in the

TABLE 3

Equilibrium in the Range of Crystallization of the Acid Trihydrated Iron Sulfate

In equilibrium with the solution are acid trihydrated sulfate $Fe_2O_3 \cdot 4SO_3 \cdot 3H_2O$ and anhydrous iron ammonium alum $NH_4 \cdot Fe(SO_4)_2$
(Average values from several experiments)

No.	Amount of $(NH_4)_2SO_4$ added	Original composition of system: 10 g $Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$, 16 cm^3 H_2O, 24 cm^3 H_2SO_4 (concentrated)								
		No. of expts.	Liquid phase			Solid phase				Distribution coefficient $K = \frac{g NH_4 \cdot 1 \cdot g OH_3 \cdot s}{g NH_4 \cdot s_1}$
			NH_4	Fe	SO_4	NH_4	Fe	SO_4	OH_3	
1	0.01	3	0.0067	0.35	63.58	0.157	19.147	68.88	6.94	K = 0.294
2	0.02	5	0.0079	–	65.40	0.186	20.0	69.74	6.92	K = 0.294
3	0.05	2	0.00885	0.347	63.00	0.21	21.07	70.08	6.895	K = 0.271
4	0.1	5	0.0121	0.237	64.88	0.38	20.3	70.32	6.72	K = 0.214
5	0.2	8	0.0136	0.107	65.72	0.744	19.51	69.72	6.335	K = 0.116
6	0.5	5	0.023	0.102	65.10	1.61	20.12	70.66	5.42	K = 0.078
7	0.7	4	0.0355	0.087	66.708	2.39	19.94	70.20	4.58	K = 0.068
8	1.0	4	0.0475	0.073	64.51	3.06	20.07	70.32	3.89	K = 0.603
9	1.2	3	0.064	0.050	–	3.8	19.51	70.32	3.12	K = 0.0525
10	1.7	2	0.128	0.049	64.97	4.8	19.54	70.20	2.068	K = 0.055
11	2.5	4	0.28	0.025	62.83	5.5	19.94	70.37	1.32	K = 0.067

alum by the oxonium ion, just as takes place in the neighboring range of crystallization of the trihydrated sulfate. As a result, the second solid phase, that of the anhydrous alum, is in this range no longer a phase of constant composition, as it was in the range of the hexahydrated sulfate.

In conformity with the proposed structural formula of the trihydrated sulfate $OH_3 \cdot [Fe(SO_4)_2]$', which shows the great similarity of this compound to the anhydrous alum, the range of crystallization of this sulfate differs considerably from the ranges of crystallization of the two sulfates considered above. Upon gradually increasing the amount of ammonium sulfate in the system, the precipitate maintains its apparent homogeneity, but the ammonium content increases not only in the precipitate but also in the liquid phase. This gives us reason to suppose that in this case there is a single solid phase in equilibrium with the solution – the isomorphous mixture of anhydrous alum and trihydrated sulfate. In fact, the distribution coefficient, calculated from Equation (2b), remains constant both in the range of small and of large amounts of ammonium in the system. With a small content of ammonium ion, when the amount of ammonium sulfate added to the system is changed from 0.01 to 0.05 g, the distribution coefficient remains almost constant. It is merely lowered slightly from the value 0.294 for 0.01 g of ammonium sulfate in the system to 0.271 for 0.05 g. Upon further increasing the amount of ammonium ion in the system, the coefficient falls rapidly to the value of 0.078 for 0.5 g of ammonium sulfate, and after that it again remains approximately constant, apparently until there is complete substitution of oxonium ions in the trihydrated sulfate by ammonium ions.

We investigated the system containing up to 2.5 g of ammonium sulfate. The distribution coefficient over this entire range of values, although it did not remain strictly constant, still showed no tendency to change in any single definite direction.

The first coefficient corresponds, apparently, to the crystalline lattice

of the trihydrated sulfate, and the second to the lattice of the anhydrous iron ammonium alum. Over this range of solid solutions which corresponded to the crystalline lattice of the anhydrous alum, there was considerable broadening of the range of solid solutions corresponding to the lattice of the trihydrated sulfate.

As for the intermediate range where there is a rapidly falling distribution coefficient, here there is either a break in the continuity of the solid solutions and the precipitate in this range is a mixture of two solid solutions, one of which corresponds to the lattice of the trihydrated sulfate and the other to the lattice of the anhydrous alum, or else in this region there takes place a continuous transition of the lattice of the trihydrated sulfate into the lattice of the anhydrous alum, and the coefficient, expressed by means of the weight percent of ions present, does not remain constant because there is a continuous and considerable change in the activity coefficients of the ions in the solid phase.

That the ammonium ions may at least partially be substituted isomorphously for the oxonium ions is shown by the following experiment.

If the system containing 2.5 g of ammonium sulfate is allowed to come to equilibrium, and 3 g of the trihydrated iron sulfate is then added, the percentage of ammonium in the liquid phase falls from 0.28 to 0.05%. This could not happen if the precipitate were not an isomorphous mixture but two solid phases, anhydrous alum and trihydrated sulfate.

SUMMARY

1. The laws for the distribution of ions between a liquid solution and solid phases have been derived for different cases which represent equilibria in heterogeneous systems.

2. It has been shown that in the case of the distribution of cations between a liquid solution and an isomorphous mixture of two salts with a common anion, the distribution law does not depend on the solubility of the solid phase or on whether only cations, or anions as well, take part in the exchange. In all systems of this kind, the distribution of the cations takes place in accordance with Nikolsky's equation, deduced for the particular case in which the solid phase is insoluble, and the anion does not exist in the liquid phase and does not take part in the exchange. Thus, this equation remains valid also for the case where the solid phase is soluble.

3. If the amount of one of the distributed components of the system is extremely small, according to this equation there must be a proportionality between the concentrations of this microcomponent in the liquid and solid phases.

4. The laws derived, as is shown by the first experiment listed, may be utilized to explain the nature of solid phases formed in heterogeneous salt solutions.

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A NEW TYPE OF TRANSFORMATION OF TERPENES

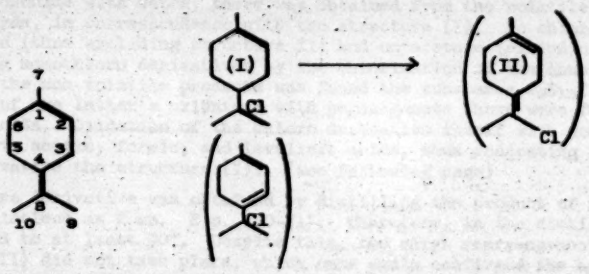
IV. THE ACTION OF CHLORINE ON TERPINOLENE AND SANTENE

D. Tishchenko and T. Danilova

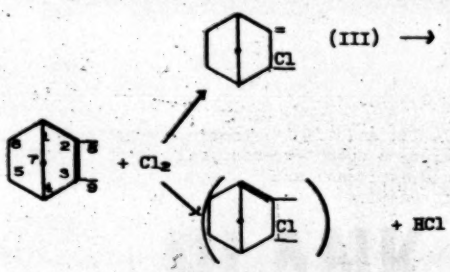
In communications I, II, and III [1] there were presented general considerations on the action of chlorine upon terpenes, and experimental data on the reaction of chlorine with α- and β-pinenes and dipentenes. In all these cases the chief and primary product of reaction was a monochloro derivative of the allyl type with a displaced double bond (monochloro derivatives of pinocarveol, myrtenol, and carveol respectively). We regarded this course of the reaction as due to the mechanism of the action of the chlorine upon quaternary olefins, to which the terpenes are analogous, and opposed the scheme of "substituent" chlorination of the American school [1].

The terpenes named above are analogous to isobutylene (β-pinene) and trimethylethylene (α-pinene, dipentene). Terpinolene and santene, having a completely branched double bond, are analogous to tetramethylethylene, as the first of these has a semicyclic, completely branched double bond (plus a cyclic double bond) and is a monocyclic terpene; the second is a bicyclic terpene, and has a cyclic completely branched double bond.

In reviewing the possible schemes of the reaction of chlorine with these terpenes, we must take account of the indicated peculiarities of their structure: in the first place, the weight to be assigned to the "anomalous" reaction in both cases must be very great, as both cases are analogous to tetramethylethylene, for which it surpasses 90% [2]; in the second place, in the case of terpinolene, the first and most important to enter into the reaction with the chlorine must be the $\Delta^{4,8}$-double bond, to form an unsaturated monochloro derivative, with the double bond shifted to the $\Delta^{8,9}$-position (great "proton similarity" of the hydrogens of the methyl groups in comparison with those of the methylene):



This direction of the reaction will be favored also by the great store of energy of the semicyclic double bond in comparison with the cyclic Δ^1; chloro derivative (I) will not tend to give an allyl rearrangement into chloro derivative (II), as the formation of the semicyclic double bond requires considerable energy; in the third place, a consideration of the stereochemical model of santene shows that its molecule is very strongly strained both on account of the formation of bridge-7 and of double bond $\Delta^{2,3}$; its isomer with the double bond in the semicyclic position $\Delta^{2,8}$ is a considerably less strained system, whereas the isomer with the cyclic double bond in the $\Delta^{1,2}$ position is under even greater strain than santene; hence it follows that the action of chlorine upon santene must proceed almost entirely according to the scheme:

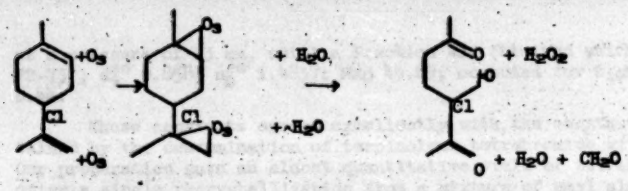


and that the chloro derivative (III), despite the presence in it of a semicyclic double bond, will not rearrange upon heating to give chloro derivative (IV), with a cyclic double bond. Because of the great steric hindrance, the formation of a saturated dichloro derivative must be almost out of the question.

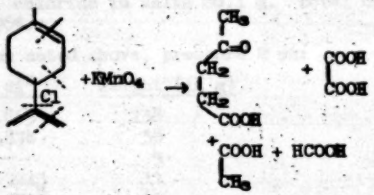
In the fourth place, as the monochloro derivative of terpinolene (I) also has two double bonds, its accumulation in the reaction mixture will result in its further reaction with chlorine to give di- and polychloro derivatives, with a corresponding decrease of its final yield (cf. the case of dipentene, communication III).

The action of chlorine on terpinolene and santene had not been studied, therefore the correctness of our hypothesis could be tested only by experiment. The reaction of chlorine with terpinolene took place under the conditions described [1]. The "anomalous" reaction took place to the extent of about 96% but the actual yield of monochloro derivative was about 50%, confirming the correctness of the hypothesis above. The structure of the monochloro derivative was shown by ozonizing and oxidizing with potassium permanganate. Upon decomposition of the ozonide with water, there was obtained from the volatile part only formaldehyde, in correspondence with the structure (I). No chloroacetone was obtained (thus excluding structure II) and no acetone (excluding all the variants forming monochloro derivatives by the chlorination of the double bond $\Delta^{1,2}$.) Among the non-volatile products was found the substance $C_9H_{13}ClO_3$. Among the products of the latter's oxidation with permanganate there were found oxalic and acetic acids. Oxidation of the chloro derivative itself with potassium permanganate gave acetic, formic, and levulinic acids, thus indicating for the monochloro derivative the structure (I): (see following page)

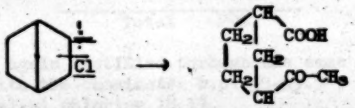
The monochloro derivative was obtained by distilling the product of chlorination of the terpinolene at 2 mm. B.p., 70-71°. Therefore, in the distilling flask, it was heated to at least 90°. Despite this, the allyl rearrangement into chloro-derivative (II) did not take place, which once again confirmed the hypotheses suggested above.



Santene was made to react with chlorine under the conditions indicated. The extent of the "anomalous" reaction was about 85%. After distillation of the excess santene in vacuum (bath temperature up to 60°) the residue crystallized. The crystals were monochloroderivatives of santene with the composition $C_9H_{13}Cl$, and were obtained in almost theoretical yield with respect to the extent of the "anomalous" reaction. Oxidation of the chloro derivative with permanganate gave a keto acid with the composition $C_9H_{12}O_3$, described in the literature [4]; from this the corresponding semicarbazone was obtained.



In order to show the presence in the monochloro derivative of the semicyclic double bond, it was ozonized; formaldehyde was found. These data lead to the structure (III) for the monochloro derivative.

(III) 

As during the isolation of the monochloro derivative (III) the chlorination products of santene were not heated above 60°, the monochloro derivative (III) must be considered as a primary product of the reaction. Heating of the monochloro derivative for 6 hours on a boiling water bath did not result in its isomerization. The monochloro derivative distilled almost completely at atmospheric pressure without change in constants; therefore, the allyl rearrangement into the chloro derivative (IV) did not take place.

In both cases, the reaction of chlorine with terpinolene and santene gave as primary products monochloro derivatives with shifted double bonds as in (I) and (III). The yields of these "anomalous" reactions, the structures of the monochloro derivatives, their thermal stability, all correspond only to our scheme for the action of chlorine on branched olefins [1] and completely confirm our present report, while opposing the "substituent" schemes of the American school. It is pertinent to point out that the monochloro derivative (III) is up to this time the only known derivative of santene whose unsaturation and carbon skeleton are the same as those of the original santene, a chloro derivative of isosantenol being so far unknown.

EXPERIMENTAL

Production of terpinolene. Several methods were tested for the production of terpinolene. As most suitable, both from the point of view of accessibility of raw material and of giving a product with the best constants, there was finally adopted a method of dehydration of terpineol by adding it drop by drop to a boiling solution of oxalic acid [5]. The crude product was distilled in a column with a theoretical equivalent of 7 to 9 plates, with a reflux ratio of 12 to 15,

at a pressure of 13 mm, until a fraction was obtained which boiled steadily at 72-73°; d_4^{20} 0.858; n_D^{20} 1.4837; MRD 45.69; computed for $C_{10}H_{18}F_2$, 45.25, E_{MRD} = 0.44.

These constants agreed excellently with the constants of terpinolene obtained by the debromination of terpinolene tetrabromide with zinc dust, [8]. Our preparation gave an almost quantitative yield of tetrabromide with m.p. 116° after a single recrystallization from a mixture of amyl alcohol and ether, and did not give the qualitative reaction for α-terpinene with nitrous acid [7].

The chlorination of terpinolene. Terpinolene 272 g, $NaHCO_3$ 130 g; oil obtained 299 g, chlorine in oil 30.1 g, chlorine in salts 28.1 g. Total chlorine 58.2 g; % of "anomalous" reaction 96%.

First distillation through column noted above, pressure 2 mm:

	B.p.	d_4^{20}	Weight (in g)
I	49-50°	0.865	138
II	50-56	0.874	38
III	57-62	-	5
IV	62-68	0.9213	11
V	68-70	0.9715	39
VI	70-71	1.0218	16.5
Residue			30.0
Loss			21.5
		Total	299

Fractions IV to VI were again distilled through the same column at 0.7 mm. A main fraction was obtained with the constants: b.p. 55-55.5°; d_4^{20} 0.988; n_D^{20} 1.5025; % Cl found, 18.6; allyl chlorine 18.1%.

Oxidation of the monochloro derivative of terpinolene. 5 g of the monochloro derivative was dissolved in acetone, cooled with snow, and stirred during the addition of an acetone solution of permanganate until there was a permanent rose color. 23 g of oxidizing agent was used up. The manganese dioxide was drawn off on a suction filter and the acetone removed from the filtrate. The MnO_2 was washed with water, again filtered off with suction, and the filtrate united with the acetone residue. The aqueous solution obtained was made acid to Congo red and steam was passed through until the distillate fraction was neutral. The distillate was neutralized (it gave a qualitative reaction for formic acid) and concentrated to 100 ml. It was then precipitated in four parts by adding silver nitrate. The precipitates were recrystallized from hot water (blackening due to HCOOH), dried, and burned. There were found: Ag 63.8, 64.1, 64.5, 64.6%; $C_2H_3O_2Ag$, computed Ag, 64.67%.

The residue from the distillation of the volatile acids was concentrated in vacuum and extracted with ether. The ether was evaporated off and the residue distilled at 1 mm. The chief fraction went over at 102-105°. A neutralization coefficient of 116 was found; that computed for levulinic acid is 116. 0.4 g of the fraction, 0.4 g of phenylhydrazine hydrochloride, and 0.6 g of sodium acetate in 30 ml of water were heated to 40°. An oil separated out rapidly, and hardened upon cooling. It was recrystallized from hot benzene until it had a constant melting point; colorless prismatic crystals with m.p. 108° were obtained. The phenylhydrazone of levulinic acid also melts at 108° [8]. The fraction gave the iodoform reaction.

Ozonation of the monochloro derivative. 3 g in chloroform was saturated with 23 liters of 6% ozone while the solution was cooled to -20°. There were obtained 4.6 g of ozonide (computed 4.7 g). The ozonide was decomposed by stirring

with ice water, with heating at the end of the reaction to 40°. The aqueous solution was found to contain formaldehyde (color reactions, precipitation with dimedon) and hydrogen chloride. The viscous precipitate insoluble in water was dried in vacuum to constant weight. Analysis: found C 51.5 and 51.5%; H 7.4 and 7.2%; Cl 13.9 and 13.7%. $C_9H_{13}ClO_3$, computed %: (respectively) 52.8; 6.3; 17.3. The substance was oxidized with an aqueous solution of permangante. Oxalic acid was found (% Ca in salt 27.5) as well as acetic acid (% Ag in salt 64.2).

Production of santene. We isolated santene by distilling the oily fractions from the Siberian fir in a column with a theoretical equivalent of about 20 plates [9]. Constants: b.p. 35-37° at 13 mm; d_4^{20} 0.8640; n_D^{20} 1.46699; MR_D found 39.18, computed 38.93. It gave a characteristic green-blue nitrosite in good yield with m.p. 125-126°.

Chlorination of santene. Santene 211.5 g, $NaHCO_3$ 210 g; oil obtained 248 g, containing 36.5 g of chlorine; chlorine in salts 25.2 g. Total chlorine 61.7 g, 82% of "anomalous" reaction. In another experiment, 86% was found. Excess santene was distilled off in a column equivalent to 7 or 8 plates at 13 mm (35 to 38°), and the residue crystallized. The crystals were dried by suction and pressed out on paper. They weighed 94.4 g, and from the liquid removed by suction 8 additional g of crystals precipitated out on cooling. Total 102 g (92% of theoretical computed on the percentage of the "anomalous" reaction). Weight of liquid removed by suction 37 g, d_4^{20} 1.168; found Cl 33.7 and 34.0%; computed for $C_9H_{14}Cl_2$ 36.8%. The liquid was cooled to -23°; crystals were obtained and pressed out on a porous plate. They melted at 88-92°, and contained 36.6 and 36.8% chlorine; therefore the substance was a saturated dichlorinated santene.

Investigation of the monochloro derivative. B.p. 40° at 3 mm, 165-167° at atmospheric pressure, with slight decomposition, m.p. 56-58°, colorless platelets. Chlorine found 21.9 and 21.7%; allyl chlorine 20.1%; computed for $C_9H_{13}Cl$, 22.6%.

Oxidation. 0.9 g of the monochloro derivative in aqueous acetone solution was oxidized at 0° with 2.42 g of $KMnO_4$. The MnO_2 was removed with suction, washed with hot water, and the filtrate added to the aqueous acetone solution. The acetone was driven off, the aqueous residue acidified to Congo red, and steam passed through. In the distillate, formic acid was found (reaction with Ag^+ and Hg^{++}). The aqueous residue was saturated with NaCl and extracted with ether. The ether was driven off from the extract to leave a viscous oil, which was allowed to react with semicarbazide acetate in aqueous solution to give a semicarbazone, which precipitated out in the form of rosette-like clusters of platelets after several hours of standing. M.p. 169-170°; the semicarbazone of the ketoacid $C_9H_{12}O_3$ is said to melt at 168° [4]. Analysis: nitrogen found 19.5 and 19.5%; computed for $C_9H_{15}O_3N_3$ 19.6%.

Ozonation of the monochloro derivative. The ozonide was obtained in the usual way. In the steam-volatile products of hydrolysis formaldehyde was detected by qualitative reactions as well as by a precipitate with dimedon. M.p. of the formaldehyde-dimedon compound, 187-188°.

SUMMARY

1. The reactions of terpinolene and santene with chlorine have been studied for the first time under conditions favoring the formation of the primary reaction products.

2. On the basis of a mechanism suggested by us for the chlorination of branched olefins [1] the predictions of yield have been satisfactorily confirmed, as well as the structure (I and III) and thermal stability of the expected monochloroterpenes. The predictions have been confirmed by experiment.

3. The "substituent" scheme of chlorination of the American school in this case, as in all the others, is not applicable.

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*See CB translation p. 593 ff.
**See CB translation p. 981 ff.
***See CB translation p. 941 ff.

A NEW TYPE OF TRANSFORMATION OF TERPENES

V. THE REACTION OF CHLORINE WITH Δ^3-CARENE

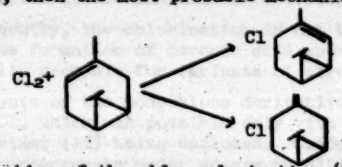
D. Tishchenko and A. Khobanskaya

Δ^3-Carene has been discovered comparatively recently in our turpentines by Krestinsky and his coworkers [1], and since then it has been shown that it is invariably present, being found in amounts from 15 to 35%. Despite this, up to the present Δ^3-carene has found no application in chemical synthesis and exists in turpentine as chemical ballast, which must be eliminated if necessary by rectification. This circumstance is explained mainly by the very slight extent of the investigation of its chemical transformations; therefore every new investigation of the chemical reactions of carene must be considered as bringing closer its chemical utilization.

The oxygenated derivatives of the carene series ($C_{10}H_{16}O$, etc.) of stable structure are unknown, just as the halogen derivatives are unknown. In the preceding communications [2] we have shown that under definite conditions, the actions of chlorine upon terpenes gives allyl monochloro derivatives of the terpenes with shifted double bonds, of the composition $C_{10}H_{15}Cl$. We have shown by the example of the monochloro derivative of dipentene that the chlorine atoms in them have a tendency toward anion exchange reactions, forming dipentene derivatives with unchanged saturation and the carbon skeleton of terpene.

The successful result of the attempts to chlorinate carene according to our method permits us to take a considerable step forward toward the discovery of practically worthwhile syntheses of carene derivatives, and possibly, to find a number of chemical applications. The present communication presents our first steps in this direction.

As we have noted, chlorinated derivatives of carene are unknown, and the action of chlorine upon carene has not been investigated. If we start with the mechanism of reaction we have suggested for chlorine and branched olefins, and turn our attention to the influence of the peculiarities of structure of the bicyclic terpenes, then the most probable mechanism of the reaction is as follows:

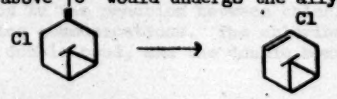


(I)

+ HCl plus dichloro derivatives

(II)

The formation of the chloro derivative (II) is improbable because of the necessity of expending energy on the formation of the semicyclic double bond. Even if the chloro derivative (II) could be formed, it would be thermally unstable, and at a temperature above 70° would undergo the allyl rearrangement.



(III)

The chloro derivative (I) formed will contribute to the conjugation of the double bond Δ^4 formed with the cyclopropane ring, which must be accompanied by the evolution of energy. For this reason, the allyl rearrangement of the chloro derivative (I) to give its allyl tautomer 5-chloro-Δ^3-carene (IV) has little probability. Consequently, the most probable primary products of the action of the chlorine on carene are the monochloro derivative (I) and a small amount of saturated dichloro derivatives. The yields of both products are determined by the relative importance of the "anomalous" reaction. In the case of α-pinene, which has a structure close to that of carene, it is approximately 60%. In the case of carene it should be higher; for in the case of α-pinene there are two obstacles to the "anomalous" reaction, that of Bredt and that of the semicyclic structure (the difficulty of forming a double bond at the head of the bridge, and the semicyclic difficulty); in the case of carene there is only the semicyclic obstacle to the formation of the chloro derivative (II); the formation of the chloro derivative (I) is favored by the conjugation of the displaced double bond with the cyclopropane ring. Therefore we should expect that in this case the relative proportion of the "anomalous" reaction will be of the same order as in the case of trimethylethylene, the prototype of Δ^3-carene, i.e., ~ 80%.

The reaction of the chlorine with carene takes place under the conditions described [2]. The relative importance of the anomalous reaction, as expected, fluctuated around 85%.

The investigation of the products of reaction was made more difficult by the thermal instability of the monochloro derivative, which decomposed to a considerable degree with the separation of hydrogen chloride at a temperature above 70°; more will be related about this separately. The yield was found by distilling the reaction product at bath temperatures not exceeding 60° and pressures of the order of 10^{-3} to 10^{-4} mm. Under these conditions, no decomposition with separation of hydrogen chloride was observed and a chlorine balance was reached for the reaction product and the fractions obtained. The monochloro derivative boiled at 27-26.5° and had the following constants: d_4^{20} 1.0095; n_D^{20} 1.5032; MR_D found 49.9. $C_{10}H_{15}Cl$ computed MR 49.10; Cl 21.2% (computed for $C_{10}H_{15}Cl$ 20.8%); all the chlorine was labile, allyl. The value of the exaltation of the molecular refraction (0.8) testified to the presence in the monochloro derivative of a three-membered ring. Conclusive evidence of this was given by the oxidation of the monochloro derivatives to gem-dimethyltrimethylenedicarboxylic (caronic) acid. The oxidation of the original carene was carried out at the same time as the oxidation of the monochloro derivative and under the same conditions. The yields of carbonic acid were comparable, thus permitting us in conjunction with the optical properties of the monochloro derivatives to consider that the presence of any considerable amounts of monocyclic chloro derivatives in the monochloro derivative would be highly improbable.

Consequently, the chlorination is not hindered by the three-membered ring in carene. The formation of caronic acid upon oxidation of the monochloro derivative is equally probable for variants of structure (I), (II), (III), and (IV).

Ozonolysis of the monochloro derivative gave a substance of the composition $C_{10}H_{15}O_2Cl$, which was possible only with variants (I), (III), and (IV), the semicyclic variant (II) being excluded. Oxidation of the monochloro derivative by potassium permanganate under severe conditions gave acetic acid in good yield; no chloroacetic acid was found, thus excluding variant (III). Because of the considerations mentioned above, variant (IV) is improbable, and we must accept structure (I) for the monochloro derivative. This is confirmed by the generally observed regularities in the reaction between chlorine and the terpene series, described in preceding communications. The chlorine atom unites to the lesser branched end of the double bond, and the double bond is shifted to a neighboring position.

We did not succeed in distilling the high boiling residue to give a pure saturated dichloride of carene; isolation was successful when the unsaturated polychloro derivatives accompanying the saturated one in the dichloride fraction were destroyed with the aid of ozone. The saturated dichloride of carene with the composition $C_{10}H_{16}Cl_2$ was a liquid, which once more (cf. Communication II) confirmed our previous opinion about the tendencies to crystallization of similar substances.

From what has been said, it is clear that the results of the experiment confirm the conclusions drawn on the basis of the mechanism suggested by us for the reaction of chlorine with branched olefins and terpenes, and again oppose the "substituent" scheme of this reaction proposed by the American school of investigators [2].

EXPERIMENTAL

Carene was isolated from resinous pine turpentine which had first been distilled in a pilot plant column and twice rectified in a laboratory column approximately equivalent to 20 theoretical plates, with a reflux ratio of 12 to 15 and a pressure of 21 mm. The fraction taken had the following constants: b.p. 74°; d_4^{20} 0.8628; n_D^{20} 1.4735; MR_D found 44.26; computed for $C_{10}H_{16}$ [Δ, 44.31; $[\alpha]_D$ + 15.3°; $[\alpha]$ = 26.6; m.p. of nitrosate 146°.

The chlorination of the carene was carried out under the conditions described [2], with cooling by ice. The yield of the "anomalous" reaction in different experiments fluctuated around 85%. We here present the data for the distillation of the reaction product at a temperature above 70°; the charge was 675 g, Cl in the oil 12.0%, total chlorine in the charge 81.0 g.

No. of fraction	Pressure, mm	Boiling point	Reflux ratio	Weight, g	d_4^{20}	n_D^{20}	% Cl	Chlorine in fraction, g
I	2	35-36°	10-12	393.0	0.8364	1.4706	–	–
II	2	35-53	10-12	38.0	0.8643	1.4784	–	–
III	1.5	53-65	10-12	13.0	–	–	–	–
IV	1.5	67-71	8	105.0	0.9873	1.5019	18.2	18.9
V	1.5	71-84	6	36.0	0.9715	1.5009	17.9	6.4
VI	1.5	84-86	5	30.0	1.0475	1.5025	24.7	7.8
Residue	–	–	–	108.0	–	–	34.5	37.3
Loss	–	–	–	27.0	–	–	–	–
								70.4

During the distillation, the separation of hydrogen chloride was observed. The loss of chlorine was 81.0-70.4 or 10.6 g, 13% of that entering the reaction. If we refer it to the monochloro derivative, about 40 g of the latter was decomposed in the distillation.

In another experiment the excess carene was distilled off through a meter herringbone column at a pressure of 0.65 mm. The boiling point of the carene was 30 to 31.5°, the bath temperature not above 65°. There was 71.0 g of chlorine in the charge, of which 70.63 g was found in the residue, which weighed 262 g. There was no loss of chlorine.

The residue was distilled in a molecular still at a pressure of 10^{-3} mm; the bath temperature was not above 65°. There were obtained:

Fraction No.	Weight, g	d_4^{20}	n_D^{20}	% Cl	Chlorine, g	Temperature of vapor
I	86.7	0.9745	1.5048	17.6	15.25	20-31°
II	27.4	0.9822	1.5031	17.8	4.87	31-32
III	25.3	1.0507	1.5038	23.1	5.84	32-53
Residue	114.6	-	-	38.0	43.50	-
Loss	4.7	-	-	-	-	-
					69.5	

No loss of chlorine was observed (charge 258.7 g, chlorine 69.6 g).

Fractions I to III from the molecular distillation were refractionated in the meter herringbone column at a pressure of 10^{-3} mm into a receiver, with a reflux ratio of 10-12. The chief monochloro derivative fraction went over at 27°, and had the constants d_4^{20} 1.0095; n_D^{20} 1.5032; Cl 21.2%.

Ozonolysis of the monochloro derivative of carene. 10 g of the monochloro derivative in 50 ml of chloroform was saturated during cooling with ice-salt mixture with 60 liters of 3.5% ozone. The ozonide solution was decomposed by stirring for 6 hours with 370 ml of water. There was practically no chloride ion in the aqueous layer (0.032 g), and the qualitative reaction for formaldehyde was negative. The chloroform was driven off from the chloroform layer, leaving 11 g of residue; this was subjected to molecular distillation. The chief fraction (3.8 g) distilled over at a bath temperature of 67° and had the following constants and composition: d_4^{20} 1.1473; n_D^{20} 1.4995; MR_D found, 51.8; Cl 17.3 and 17.6%; C 59.5 and 59.4%; H 7.1 and 7.2%; For the chloroketoaldehyde $C_{10}H_{15}ClO_2$ the calculated values are: MR_D 51.7; Cl 17.5%; C 59.2%; H 7.4%.

The oxidation of the monochloro derivative of carene, and at the same time, of the original carene to caronic acid [4]. 20 g portions of each were oxidized by stirring on a water bath during the addition of a solution of 140 g of $KMnO_4$ in 3.5 liters of water. Decoloration took 44 hours. The solution had steam passed through, and the manganese dioxide was filtered off with suction. The solution was concentrated in a stream of carbon dioxide to 300 ml, neutralized with hydrochloric acid, and the oxalic acid precipitated with calcium chloride. The precipitate was filtered with suction, the solution acidified to Congo red, and treated with ether for 48 hours in an extractor. The ether was driven off from the extract, and the residue allowed to crystallize. 2.5 g were obtained from the carene, and 2.0 g from the monochloro derivative. In both cases, the crystals were washed with benzene, pressed on a porous plate, and recrystallized from hot water to a constant m.p. of 174-175° in both cases. This corresponded to the cis-caronic acid [4]. From the acid obtained by oxidizing the monochloro derivative, the ammonium salt was prepared, and its nitrogen content determined. N found 15.2%; computed, 14.6%.

The monochloro derivative of carene (4 g) was oxidized once more under the same conditions. The aqueous solution of the oxidation products had steam passed through to remove neutral substances, was then acidified to methyl orange, and had steam passed through again until the distillate was neutral. The distillate was titrated with alkali. Total volatile acids, calculated as acetic, amounted to 0.96 g (1.4 g could have been obtained). The solution was evaporated to 30 ml and precipitated in three portions with the computed amount of silver nitrate. The precipitate was filtered with suction, and recrystallized from hot water. The silver content in it was found to be 64.3, 64.4, and 64.4%. Computed for $C_2H_3O_2Ag$, 64.6%.

During the distillation of the high-boiling residue from one of the experi-

experiments on the chlorination of carene, a fraction was obtained which contained about 36% of chlorine. This was saturated with ozone, treated with water, and the residue insoluble in water distilled to give a fraction with b.p. 97 to 101° at 11 mm, with 33.4% Cl, 58.4% C, and 7.7% H. The dichloroderivative of carene, $C_{10}H_{16}Cl_2$, contains 34.6% Cl, 58.4% C, and 7.5% H. The substance was a liquid.

SUMMARY

1. The action of chlorine on Δ^3-carene has been studied for the first time.

2. It has been shown that the primary products of this reaction are the monochloro derivative of carene with a shifted double bond (3-chloro-Δ^4-carene; main reaction ~80 to 85%) and a saturated carene dichloride (side reaction ~20 to 15%).

3. These results are in accordance only with the mechanism for the reaction of chlorine with branched olefins suggested by us, and contradict the "substituent" scheme of chlorination of the American school.

4. A preliminary consideration of the possible results of this reaction from the point of view of our mechanism, and of the peculiarities of structure of the carene, permitted us to make a correct prediction of the structure of the monochloro derivative and the relative amount of the "anomalous" reaction.

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*See CB translation p. 563 ff.

**See CB translation p. 1027 ff.

ON THE RELATIONSHIP BETWEEN THE PHYSICAL CHEMICAL PROPERTIES OF ORGANIC COMPOUNDS AND THE STRUCTURE OF THE MOLECULES

III. THE BOILING POINTS OF PHENOLS

N. Kozlov

Molotov State Pedagogical Institute

In the present work, we have subjected to investigation the boiling points of the phenols and of their ethers and esters, from the point of view of the predictions we made in our previous communication [1].

First we calculated the coefficients of the basic structural elements or functional groups of the compounds investigated; their values are listed in Table 1.

TABLE 1

Functional group	OH	OCH_3	OC_2H_5	$OCOCH_3$
Value of the coefficient (in °)	102	74.5	90.0	115

The value of the coefficients for the benzene nucleus, hydrocarbon radicals, and halogens remains the same as in the preceding communication.

Then we calculated the coefficients influencing the boiling point (computed on the basis of additivity) of mutually acting combinations of substituents depending on their chemical nature and their position in the benzene nucleus. The data obtained are listed in Table 2.

We utilized the coefficients we had obtained, and the formula we had proposed:

$$T = A_n + B_n + C_n + D_n \ldots + (a_n + \ldots), \qquad (1)$$

where T is the calculated boiling point of the organic compound; A, B, C, D ... are the coefficients of the structural elements; a, b, ... are the coefficients of mutual influence of combinations of substituents upon the boiling point; n is the number of identical structural elements or of identical combinations of substituents needed to calculate the boiling points of the phenols and their ethers and esters. The results obtained are listed in Tables 3, 4, and 5.

The experimental data on the boiling points of phenols and their derivatives, which are listed for the purpose of comparison with the calculated data, were taken from the reference books of Beilstein [2] and Heilbron [3].

The data of Tables 3, 4, and 5 completely support the coefficients we have proposed, as well as the formulas for the calculation of the boiling points of phenols and their derivatives, seeing that the theoretically calculated boiling points coincide almost completely with those found experimentally.

Previously, we had already expressed the idea that the coefficients we had suggested for the mutual influence of substituents were to a considerable

extent measurements of the influence exerted on the physicochemical properties of the compound by intramolecular interaction of the substituents. Here, therefore, we consider it necessary to subject these suggested coefficients to analysis.

Excluding a single case, all the coefficients are negative. Only for the combination of the groups OH and OH, and then for the single case where these are in the para position, do we have a coefficient with a positive value. The cause for this apparently lies in the fact that hydroxyl groups in the para position have a special sort of interaction in comparison with hydroxyls in the ortho and meta positions. Here there undoubtedly take place as well various fine structural changes in the hydroxyl groups.

TABLE 2

Combination of substituents	Positions of substituents		
	Ortho	Meta	Para
OH–CH_3	-19	-9.6	-10.6
OH–C_2H_5	-31.1	-24.1	-19.1
OH–C_3H_7 n	-36.2	-33.2	-29.2
OH–C_3H_7 iso	-40.4	-26.4	-25.4
CH_3–OCH_3	-14.1	- 8.6	- 8.6
CH_3–OC_2H_5	-15.6	- 8.6	-10.6
OH–OH	-42	- 8	+ 2
OH–OCH_3	-51.5	-12.5	-13.5
OCH_3–OCH_3	-23	-15	-16
CH_3–$OCOCH_3$	-17.6	-13.6	-12.6
OH–Cl	-57	-19	-16
OH–Br	-63	-22	-20
OCH_3–Cl	-10.5	-7.5	-7.5
OC_2H_5–Cl	-11	-10	-10
OCH_3–Br	-12.5	-16.5	-15.5

The combination of the groups CH_3 and OH shows a very great influence on the boiling point, lowering the calculated amount considerably in comparison with what would be found if mere additivity were valid. The greatest influence is observed in the case where these substituents are in the ortho position. It must be strongly emphasized that an increase in the number of carbon atoms in the alkyl interacting with the hydroxyl group favors an increase in influence on the boiling point. But in this case, when we pass from the methyl to the propyl, the difference in the degree of influence in relation to position of the substituents in the nucleus begins to decrease, and becomes almost completely identical for substituents in the ortho, meta, and para positions.

If in the mutually interacting substituent pair OH and CH_3 we substitute active hydroxyl hydrogen on the CH_3 group, we observe a sharp change in the extent of influence of the group on the boiling point. An even greater change is observed in the case where the active hydrogens of two interacting hydroxyl groups are substituted by alkyl.

On the basis of everything said above, we may draw the following conclusions.

1. The suggested formula and coefficients are suitable for the calculation of the boiling points of phenols and their ethers.

2. The method suggested by us for investigating the boiling points of organic compounds makes it possible to determine the laws of change of the boiling point in a number of phenols in relation to the structure of their molecules, and is capable of deciding questions of practical significance. Thus, for example, in the case where different and conflicting experimental data have been found, for one and the same compound by different authors, we may determine the most nearly correct. Thus, of the two experimental results for the boiling point of 2,3,4,5-tetramethylphenol, 245-250° and 260.0°, the second figure must be accepted as correct; of the figures 205-206° and 212-213° for 2,4,5-trimethylphenol, the first must be taken as correct. Similar conclusions may be made with regard to the boiling points of 3,5-dimethoxytoluene, 2,6-dihydroxymesitylene, etc. (cf. the data of Tables 3, 4, and 5).

Further, the method we have suggested makes it possible to detect and correct erroneous experimental data on the boiling points of phenols. Thus,

TABLE 3

Boiling Points of Mono-, Di-, and Tri-Substituted Phenols

Name of phenol	Boiling point	
	Experimental	Calculated
2,3-Dimethylphenol	218°	217.8°
2,4-Dimethylphenol	212	211.5
3,4-Dimethylphenol	225	226.2
3,5-Dimethylphenol	220	222.0
2,5 Dimethylphenol	211.5; 213.5	211.7
2,6-Dimethylphenol	203	203.0
	211-213	
2,3,4-Trimethylphenol	235-237	239.0
3,4,5-Trimethylphenol	248-249	248.5
2,4,5-Trimethylphenol	230-232	233.0
2,3,5-Trimethylphenol	230-231	234.0
2,4,6-Trimethylphenol	220.0	219.0
2,3,4,5-Tetramethylphenol	246.5; 260.0	258.5
2,3,5,6-Tetramethylphenol	249.0	244.0
Pentamethylphenol	267.0	266.5
2-Ethylphenol	195-197	207.0
	196-199	
	207	
2,4-Diethylphenol	228-230	234.0
2,6-Diethylphenol	238-240	221.0
2-Methyl-4-ethylphenol	224	225
4-Methyl-2-ethylphenol	216-218	222
3-Methyl-4-ethylphenol	228-229	238
2-Methyl-6-ethylphenol	212-214	213.5
2,6-Dimethyl-4-ethylphenol	228-230	230.0
2,4-Dimethyl-5-ethylphenol	242-244	237.5
2,4-Dimethyl-6-ethylphenol	228-230	226.0
2,3,4-Trimethyl-6-ethylphenol	250-252	249.5
3-Methyl-4,6-diethylphenol	247-249	248.0
4-Methyl-2,5-diethylphenol	248-250	244.0
2-Methyl-4,6-diethylphenol	234-236	234.5
4-Methyl-2,6-diethylphenol	229-230	231.0
3,4-Dimethyl-2,6-diethylphenol	246-248	249.0
2,3-Dimethyl-4,6-diethylphenol	244-246	251.5
2,4-Dimethyl-3,6-diethylphenol	250-252	243.0
4-Methyl-2,3,6-triethylphenol	242-244	246.5
2-Methyl-3,4,6-triethylphenol	252	251.0
3-Methyl-2,4,6-triethylphenol	256-258	249.7
2-Methyl-4-n-propylphenol	239-240	237.5
2,4-Dimethyl-6-n-propylphenol	243-245	240.0
2-Methyl-4-isopropylphenol	227-229 231.0	233.0
2-Methyl-6-isopropylphenol	225-226	228.0
	228-230	
3-Methyl-4-isopropylphenol	237;244	243.0
3-Methyl-5-isopropylphenol	241.0	241.0
4-Methyl-3-isopropylphenol	228-229	241.0
2,3-Dihydroxytoluene	238-241	244.0
2,4-Dihydroxytoluene	267-270	277.0
3,4-Dihydroxytoluene	251-252	254.0
3,5-Dihydroxytoluene	287-289	287.5
2,6-Dihydroxy-p-xylene	277-278	280.0
2,6-Dihydroxymesitylene	274-275	265.5
Pyrogallol	292-294	294.0

TABLE 4

Boiling Points of Phenol Ethers

Name of ether	Boiling point	
	Experimental	Computed
2,3-Dimethylanisol	195°	196°
2,4-Dimethylanisol	191	191
2,5-Dimethylanisol	189-190, 194	190
2,6-Dimethylanisol	182	185.5
3,4-Dimethylanisol	201-202;204-205	202
3,5-Dimethylanisol	195-195	196.5
2,4,5-Trimethylanisol	209-211; 214	213.5
2,4,6-Trimethylanisol	203-204	203.5
3,4,5-Trimethylanisol	226-227	225.0
2,3,5-Trimethylanisol	213-216	213.5
2,3-Dimethylphenetol	210;218	210.0
2,4-Dimethylphenetol	202-203	203
2,5-Dimethylphenetol	202-203	203.0
2,6-Dimethylphenetol	195-196	198.0
3,4-Dimethylphenetol	215-218	215.0
3,5-Dimethylphenetol	210	212.0
2,4,5-Trimethylphenetol	212-213; 223-226	225.5
2,4,6-Trimethylphenetol	208;217	214.0
3,4,5-Trimethylphenetol	237-238	238.5
2,3,4,5-Tetramethylphenetol	236-237	239.5
3-Methyl-6-hydroxyanisol	209	212.0
3-Methyl-6-hydroxyanisol	217-219; 221-222	216.5
4-Methyl-2-hydroxyanisol	217-218; 222-223	217.5
2,3-Dimethoxytoluene	202-203; 211	214.0
3,4-Dimethoxytoluene	216-218	219.5
2,5-Dimethoxytoluene	214-218	221
3,5-Dimethoxytoluene	227-228; 244	227.5
1,2,3-Trimethoxybenzene	235; 241	242
1,2,4-Trimethoxybenzene	245-247	249.5
1,3,5-Trimethoxybenzene	255.0	258
3,4,5-Trimethoxybenzene	236-237	247.5
1,2,3,4-Tetramethoxybenzene	271.0	263.0
1,2,3,5-Tetramethoxybenzene	271.0	271.0
3-Hydroxy-4,5-dimethoxytoluene	239.0; 265.0	244.0
1,2-Dihydroxy-3,4-dimethoxybenzene	238.0	280.0
5-Hydroxy-4-methoxy-m-xylene	227-228	222.5
3-Methoxy-4-ethyltoluene	200	202.7
3-Methoxy-4-ethyl-o-xylene	216-218	217.5
5-Methoxy-4-ethyl-o-xylene	218-219	222.7
4-Methoxy-5-ethyl-o-xylene	210-211	210.2
5-Methoxy-2,4-diethyltoluene	222-224	231.5
4-Methoxy-2,5-diethyltoluene	234-236	233.5
6-Methoxy-3,6-diethyl-o-xylene	234-236	237.5

2,3-dimethoxytoluene has a boiling point not of 203.0°, as determined experimentally, but of 214.0°; 4-methyl-3-isopropylphenol has a boiling point not of 228-229°, as determined experimentally, but of 241°, etc.

In addition, this method makes it possible to calculate the boiling points of unsynthesized compounds of the phenol series on the basis of their structural formulas. Thus, for example, the boiling point of 4-methyl-2,3,5-tri-

TABLE 5

Boiling Points of Acetate Esters of Phenols

Name of ester	Boiling point	
	Experimental	Computed
3-Acetoxy-o-xylene	226-228°	228°
4-Acetoxy-o-xylene	235	234
2-Acetoxy-m-xylene	213-214	219
4-Acetoxy-m-xylene	224-226	224
5-Acetoxy-p-xylene	237.0	222.0
1-Acetoxy-2,3,4-trimethylbenzene	245-246	241.5
1-Acetoxy-2,3,5-trimethylbenzene	241	240.5
1-Acetoxy-2,4,6-trimethylbenzene	245-246	241.5
2-Acetoxy-1,3,5-trimethylbenzene	236	233.0

ethylphenol must equal 266°, that of pentamethylanisol 253.0°, that of pentamethylphenetol 264.0°, and that of pentamethylacetoxybenzene 273.0°, etc.

II

During the investigation of the boiling points of halogen derivatives of phenol we found by means of our method new and very valuable properties. These are further indications of its ability to indicate, in a new way, the presence of intramolecular hydrogen bonds in organic compounds.

In accordance with the method described above, we calculated a list of boiling points of various halogen derivatives of phenols; the results are given in Table 6, column 3.

In looking over the data of Table 6, we are struck by the following fact: the boiling points of entire series of compounds fail to agree with those calculated by our method. Among these phenols are all the chlorine derivatives in which there are three or more substituents, with one or two atoms of chlorine in the ortho position to hydroxyl. In the case where there are di- or trichloro-substituted phenols, with the atoms of chlorine in the meta or para positions to the hydroxyl, the theoretically calculated boiling point agrees with that found experimentally. Thus, the cause of the deviation must be sought in the character of the influence on the boiling point due to the interaction of the hydroxyl and chlorine groups when these are in the ortho position.

These two substituents are strongly polar, and when they are in the ortho position in the benzene nucleus, they interact in a special way, as is shown by the specific influence on the general physico-chemical properties of the compound. We may now conclude that here there takes place the formation of an intramolecular hydrogen bond, which has the sort of influence related to the so-called "ortho-effect" [4].

The "ortho-effect" is detected by virtue of the very considerable decrease of the boiling point as compared with that calculated on the basis of additivity; this decrease equals 57.0°. Such a considerable lowering of the boiling point is a phenomenon of a special kind which reveals the strong interaction of these substituents, resulting in a change in the substituents themselves.

We must therefore accept the fact that when a chlorine atom enters a phenol in the ortho position, the interaction of the chlorine with the hydroxyl to some degree changes the structure of the hydroxyl group, and lowers the boiling point by 57.0° in comparison with the computed boiling point. Therefore, when a second

TABLE 6

Boiling Points of Halogen-Substituted Phenols

Name of phenol	Boiling point		
	Experimental	Calculated	
o-Chlorophenol	176°	176°	–
m-Chlorophenol	214; 216	214	–
p-Chlorophenol	217; 219	217	–
2,3-Dichlorophenol	–	206	218°
3,4-Dichlorophenol	206-208; 210	208	210
2,5-Dichlorophenol	211	200	212
2,6-Dichlorophenol	218-220	162	219
2,4-Dichlorophenol	245-246; 253	222	–
3,5-Dichlorophenol	233	238	–
2,3,4-Trichlorophenol	–	–	260
2,3,5-Trichlorophenol	253	222	245
2,3,6-Trichlorophenol	–	–	263
2,4,6-Trichlorophenol	244	181	245
2,4,5-Trichlorophenol	271	271	–
2,3,4,5-Tetrachlorophenol	–	–	276
2,3,4,6-Tetrachlorophenol	278	201	277
2,3,5,6-Tetrachlorophenol	–	–	279
Pentachlorophenol	289; 310	213	309
2-Methyl-3-chlorophenol	225	223	–
2-Methyl-4-chlorophenol	220-225; 237	228	–
2-Methyl-6-chlorophenol	185; 189	187	–
2-Methyl-5-chlorophenol	225	225	–
3-Methyl-2-chlorophenol	196	194	–
3-Methyl-4-chlorophenol	235;238	235	–
3-Methyl-5-chlorophenol	–	234	–
3-Methyl-6-chlorophenol	196-197	197	–
4-Methyl-2-chlorophenol	195	195	–
4-Methyl-3-chlorophenol	228	231	–
3-Methyl-4,6-dichlorophenol	232	238	–
4-Methyl-2,6-dichlorophenol	–	237	–
2-Methyl-4,6-dichlorophenol	–	219	–
3-Methyl-2,4,6-trichlorophenol	265	234	279
3,5-Dimethyl-4-chlorophenol	232	251.5	–
3,5-Dimethyl-5-chlorophenol	–	257	–
2,4-Dimethyl-6-chlorophenol	221	203.5	–
2-Chloro-1,4-dihydroxybenzene	263	261	–
4-Chloro-1,4-dihydroxybenzene	259	259	–
2,4-Dichloro-1,4-dihydroxybenzene	254	199	254
o-Bromophenol	194-195	195	–
m-Bromophenol	236-238	236	–
p-Bromophenol	238	238	–
2,3-Dibromophenol	–	242	–
2,4-Dibromophenol	238; 243-246	240	–
2,5-Dibromophenol	–	239	–
2,6-Dibromophenol	–	260	–
3,4-Dibromophenol	–	285	–
3,5-Dibromophenol	274-276	279	–
2,4,6-Tribromophenol	282-290	231	294
2-Methyl-3-bromophenol	–	241	–
2-Methyl-4-bromophenol	235	246	–
2-Methyl-5-bromophenol	–	244.5	–
2-Methyl-6-bromophenol	200	203	–

TABLE 6 Continued

Name of phenol	Boiling point		
	Experimental	Computed	
3-Methyl-2-bromophenol	210	209	-
3-Methyl-5-bromophenol	-	253	-
4-Methyl-2-bromophenol	214; 218-219	211.5	-
4-Methyl-3 bromophenol	245	249	-
2-Methyl-3,5-dibromophenol	233-237	281	-
2-Methyl-4,6-dibromophenol	263-266	244	-
4-Methyl-2,6-dibromophenol	268-271	210	272
4-Methyl-3,5-dibromophenol	280-285	286	-
2,4-Dimethyl-6-bromophenol	228-230	217.5	-
o-Chloroanisol	195-196	195	-
m-Chloroanisol	193-194;198-202	198	-
p-Chloroanisol	198	198	-
2,3-Dichloroanisol	-	236.5	-
2,4-Dichloroanisol	232-234	230.5	-
2,5-Dichloroanisol	-	230.6	-
2,6-Dichloroanisol	-	227.5	-
3,4-Dichloroanisol	-	239.5	-
3,5-Dichloroanisol	-	233.5	-
2,4,6-Trichloroanisol	240	255	-
3,4,5-Trichloroanisol	256	273	-
2-Methyl-3-chloroanisol	213-214	211.5	-
2-Methyl-4-chloroanisol	212-214	213.5	-
2-Methyl-5-chloroanisol	212-213	213.5	-
2-Methyl-6-chloroanisol	-	210.5	-
3-Methyl-2-chloroanisol	218	214	-
3-Methyl-5-chloroanisol	-	-	-
3-Methyl-6-chloroanisol	212-215	216	-
4-Methyl-2-chloroanisol	210-215;215-218	216	-
4-Methyl-3-chloroanisol	212	217	-
2-Methyl-4,6-dichloroanisol	230	250.5	-
3-Methyl-4,6-dichloroanisol	249	248	-
4-Methyl-2,5-dichloroanisol	234	248.5	-
4-Chloro-2-hydroxyanisol	235;236-243	229.5	-
5-Chloro-2-hydroxyanisol	241-243	232.5	-
4,5-Dichloro-2-hydroxyanisol	260-270	250	-
3,4-Dimethoxychlorobenzene	242	239	-
1,4-Dimethoxy-2,6-dichlorobenzene	259	271	-
o-Chlorophenetol	208-210	210	-
m-Chlorophenetol	204-205;210-211	211	-
p-Chlorophenetol	210-212	211	-
2,3-Dichlorophenetol	-	249	-
2,4-Dichlorophenetol	236-237	243	-
2,5-Dichlorophenetol	-	243	-
2,6-Dichlorophenetol	-	242	-
3,4-Dichlorophenetol	-	250	-
3,5-Dichlorophenetol	-	244	-
2,4,6-Trichlorophenetol	246;266	267	-
2-Methyl-3-chlorophenetol	-	223	-
2-Methyl-4-chlorophenetol	-	225	-
2-Methyl-5-chlorophenetol	210-220	225	-
2-Methyl-6-chlorophenetol	-	224	-

TABLE 6 Continued

Name of phenol	Boiling point		
	Experimental	Computed	
3-Methyl-2-chlorophenetol	–	229°	–
3-Methyl-5-chlorophenetol	–	232	–
4-Methyl-2-chlorophenetol	233-238°	229	–
4-Methyl-3-chlorophenetol	–	228	–
o-Bromoanisol	217-218; 221-223	218	–
m-Bromoanisol	210-214	214	–
p-Bromoanisol	215-223	215	–
2,4-Dibromoanisol	258-262; 272	267	–
3,5-Dibromoanisol	257-262	262	–
2,4,6-Tribromoanisol	297-299	309	–
3,4,5-Tribromoanisol	300-311	309	–
2,3,4,6-Tetrabromoanisol	338-342	342	–
3-Methyl-2-bromoanisol	–	243.8	–
4-Methyl-2-bromoanisol	225-227	236.5	–
5-Methyl-2-bromoanisol	–	257.5	–
6-Methyl-2-bromoanisol	–	251	–
2-Methyl-3-bromoanisol	–	244	–
4-Methyl-3-bromoanisol	222	210	–
5-Methyl-3-bromoanisol	–	243	–
2-Methyl-4-bromoanisol	–	248	–
3-Methyl-4-bromoanisol	225	249	–
2-Methyl-3,5-dibromoanisol	268-272	269.5	–
2-Methyl-4,6-dibromoanisol	267	277	–
4-Methyl-2,5-dibromoanisol	274-277	277	–
4-Methyl-2,6-dibromoanisol	262-264	285	–
2-Methyl-3,4,5-tribromoanisol	320	312	–
2-Methyl-3,4,6-tribromoanisol	308-311	311	–
3-Methyl-2,4,6-tribromoanisol	319-320	316	–
3-Methyl-2,3,5-tribromoanisol	311-313	313	–
4-Methyl-2,3,6-tribromoanisol	320	316	–

chlorine atom enters the other position ortho to the hydroxyl, it finds a hydroxyl group which has been changed by the action of the first chlorine atom, and being unable to change this action, behaves toward it as toward a new substituent. That is why the entrance of the second chlorine atom into a position ortho to the hydroxyl cannot result in the same sort of decrease in the boiling point as the entrance of the first atom of chlorine. This fact may be clearly seen when the boiling points of the chlorine-substituted ortho-chlorophenols are considered. Thus, in 2,6-dichlorophenol, the first chlorine atom, by its interaction with the hydroxyl results in a lowering of the boiling point by 57.0°, but the introduction of a second chlorine atom results in a lowering by only 7.0°. In 2,6-dichlorophenol the total lowering of the boiling point equals 64.0°, which is in a way the combined effect of the influence of the first chlorine atom's interaction with the hydroxyl, equal to 57.0°, and of the influence of the two chlorine atoms acting upon each other in the meta position, for which the coefficient equals 8.0°. Consequently, no influence of the action of the second chlorine atom upon the hydroxyl group is observed, while the influence of the interaction with the chlorine atom is observed. Here we observe the "disappearance" of several properties of the hydroxyl group, we note its lack of ability to interact with other substituents with the strength inherent in the free hydroxyl group. These

facts undoubtedly indicate the presence in the ortho chlorophenol of a hydrogen bond, which can also be detected by our method of investigating boiling points, and can even be characterized by a new constant – the coefficient of lowering of additively calculated boiling points.

From all this it follows that in such a case, the coefficient for the mutual influence of the second chlorine atom which is in the ortho position to the hydroxyl is zero, while the coefficient of mutual influence of this chlorine atom with other substituents remains as before.

Further, if a second chlorine atom is substituted in the meta position in orthochlorophenol, then its coefficient of mutual influence with the hydroxyl will equal 7.0°. This will also be a secondary coefficient for the mutual influence of OH and Cl in meta positions in compounds in which there is already a chlorine atom in the ortho position with regard to the hydroxyl. The secondary coefficient of mutual influence on the boiling point of OH and Cl in the para position, in compounds in which there is already a chlorine atom in the ortho position with regard to the hydroxyl, equals 9.0°.

Utilizing the secondary coefficients, we recalculated the boiling points of the chlorine-substituted orthochlorophenols. The data obtained are listed in Table 6, column 4. These latter calculations show that all the compounds whose boiling points deviated considerably from the computed now completely correspond to those computed theoretically.

We encounter a completely analogous phenomenon in our investigation of the boiling points of the bromine derivatives of phenol. In ortho bromophenol there is also the formation of a hydrogen bond; that is why the bromine-substituted phenols also require the use of secondary coefficients.

Thus, in our study of the relationship between the structure and the b.p.'s of organic molecules, we encounter two kinds of mutual influence of the substituents on the boiling point. In the first case, the substituents in the benzene nucleus act upon each other in such a way as to leave the substituents themselves apparently completely unchanged, so that they can at the same time interact with other substituents, maintaining the values of their coefficients unchanged. Consequently, in a very considerable number of the compounds investigated – the aromatic hydrocarbons, halogen derivatives, phenols – the mutual action of two substituents is not accompanied by a noticeable change in the properties and structure of the interacting substituents, despite the simultaneous action upon them of other substituents. In the second case, as in the ortho halogen-substituted phenols, we encounter a change in the properties of the substituents as a result of their interaction with each other. This is detected as a result of the inability of several substituents in the presence of other substituents to interact with new groups with the force inherent in the free, unchanged substituent.

And finally, it is of interest to note that the methylation or ethylation of ortho chlorophenol or its substituted derivatives nullifies the "ortho effect". The mutual action of the methoxy or ethoxyl groups with an atom of chlorine in the ortho position does not change its value and in the presence of other substituents, the use of secondary coefficients becomes superfluous.

The considerable lowering of the boiling points observed as a result of the interaction of the OH — OH and the OH — OCH_3 groups in the ortho position in the benzene ring lends considerable probability to our hypothesis of the presence of hydrogen bonds in pyrocatechol and ortho-methoxyphenol.

Thus, the method we have suggested for investigating the relationship between the boiling points of organic compounds and the structure of their molecules

not only makes it possible to discover the chief laws determining the change in the boiling point in the phenol series, but is very suitable for the discovery of definite structural changes in the substituents as a result of their interaction within the organic molecule itself. Several obstacles to the understanding of the interaction of the substituents within the molecule in the phenol series have genuine significance, and are concretely manifested in the formation of the hydrogen bond.

Further, we can make several practical observations on the boiling points of certain chloro-substituted phenols, which from our point of view, are erroneous. Thus, we must assume that the boiling point of 3,4,5-trichloroanisol is not 256.0°, as determined experimentally, but 273.0°; of 2-methyl-4,6-dibromophenol not 263-266°, but 244.0°. The data for the boiling points of 3-chloro-2-hydroxytoluene and 4-chloro-3-hydroxytoluene, listed in the hand book of physico-chemical values [5], are completely unreliable, and should be corrected.

SUMMARY

The method of investigation of the boiling points of organic compounds suggested by the author makes it possible to determine the relationship between boiling point and structure of the molecule in the phenol series, and to utilize this in solving a number of questions of theoretical and practical value.

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*See CB translation p. a-111 ff.

ON THE RELATIONSHIP BETWEEN THE PHYSICAL CHEMICAL PROPERTIES OF ORGANIC COMPOUNDS AND THE STRUCTURE OF THEIR MOLECULES

IV. THE BOILING POINTS OF ALCOHOLS AND ETHERS OF THE PARAFFIN SERIES

N. Kozlov

Molotov State Pedagogical Institute

A. The Boiling Points of Alcohols

It is a fact that alcohols of a saturated nature have a very great value both in organic synthesis and in chemical industry. As methods of synthesis and knowledge of their properties has developed, their role in industry has increased continuously from year to year.

All this explains the interest in the investigation of the physico-chemical properties of the alcohols generally and in their boiling points in particular. But work already done in this field [1,2,3] must be regarded as only the first attempts at investigating the boiling points of alcohols, as the chief object of investigation, the knowledge of the laws determining the boiling points in the alcohol series, was not achieved. In view of the considerable importance of this question from the scientific and practical points of view, we decided to utilize the results of our investigations [4] of the boiling points of the methane hydrocarbons along with our methods of analysis to investigate the boiling points of alcohols.

In conformity with our hypotheses, which have been presented in previous communications, the homologous series of primary alcohols with normal structure, were regarded as compounds having a very simple structural relation to their isomers. Therefore we regarded the boiling points of the primary alcohols with normal structure as the basis for a study of the boiling points of the alcohols with iso structures.

We took the following data on the boiling points of the primary alcohols from already extant experimental results. They are listed in Table 1.

TABLE 1

Alcohol	Boiling point	Homologous difference
Methyl...	65°	–
Ethyl ...	78	13
n-Propyl.	98	20
n-Butyl..	118	20
n-Amyl...	138	20
n-Hexyl..	157	19
n-Heptyl.	176	19
n-Octyl..	194	18
n-Nonyl..	213	19
n-Decyl..	231	18

The data listed (Table 1) indicate the complete regularity of the change of boiling point in the homologous series of primary alcohols, the boiling point rising by almost the same value in passing from one homolog to the next.

Next, by comparing the boiling points of the alcohols with iso structure with the boiling points of the primary alcohols of normal structure, we found

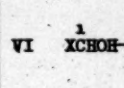
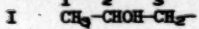
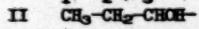
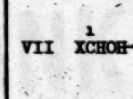
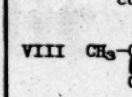
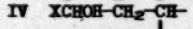
that a definite change in the structure of the chain or a shift in the position of the hydroxyl group corresponded to a definite change in the boiling point of the alcohol of normal structure.

This was observed both during the displacement of the hydroxyl group from a terminal carbon to the middle of the chain, as well as in the case where a methylene group was transformed into a methyl side chain.

The values of the structural factors found by us, and their influence on the boiling point are listed in Table 2.

TABLE 2

Corrections of Boiling Point with Regard to Boiling Point of Normal Primary Alcohols of the Same Composition

Structural factor	Value of correction	Structural factor	Value of correction
Depending on position of hydroxyl group			
I 	-18°	VI	-20°
II 	-21°		
and so on without change of coefficient		VII	-16°
Depending on position of methyl group		and so on without change of coefficient	
III	-10°	VIII 	-16°
IV	- 8°	IX	-13°
V 	- 6°		
and so on without change of coefficient		(where X is a hydrogen atom or a hydrocarbon radical).	

In addition to these values, the coefficient for the influence on the boiling point of the combined action of two methyl groups on neighboring carbon atoms retains the earlier given value of +5°.

Thus, we have shown that definite structural groups present in the alcohol molecules have definite types of relations with each other, to an extent which depends on their relative position in the molecule. If the extent of influence is determined by the values of the coefficients introduced by us above, then in this case we may note that the influence of the hydroxyl group is increased in proportion as it is displaced inside the carbon chain, and the influence of the methyl group is the greater the closer it is situated to the hydroxyl.

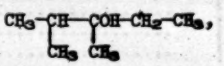
As the influence of the structural factors has a strictly regular character and in practice retains its value in alcohols with different contents of carbon

atoms, we may express this relation in mathematical form, and calculate the boiling points of alcohols of iso structure from the following formula:

$$T' = T - (A_n + B_n + C_n \ldots\ldots\ldots), \qquad (I)$$

where T is the boiling point of the primary alcohol of normal structure, T' the boiling point of the alcohol with iso structure and the same number of carbon atoms, A, B, and C are the coefficients for the structural factors and the mutual influences of the groups, n is the number of identical structural factors and group combinations.

The method of calculation can be shown clearly by the calculation of the boiling point of 2,3-dimethylpentanol-3,



which, according to the experimental data, has a boiling point of 138°. In considering the structure of this compound, we note in its molecule the following structural factors:

1) A hydroxyl group upon the third carbon atom, which causes a lowering of 21°.

2) A methyl group upon the carbon atom in position 3, to which the hydroxyl group is also attached; this results in a lowering of 13°.

3) A methyl group upon carbon atom 2, in a position alpha to the hydroxyl; this causes a lowering of 10°.

4) Methyl groups upon carbon atoms 2 and 3, neighboring carbon atoms; this causes a rise of 5°.

As the boiling point of n-primary heptyl alcohol is 176°, then on the basis of the proposed formula (I), the calculated boiling point of 2,3-dimethylpentanol-3 will equal:

$$T = 176 - (21 + 13 + 10) + 5 = 137°.$$

Utilizing the suggested formula (I), and the corrected coefficients, we carried out the calculation of boiling points of alcohols of the most varied structure. The results obtained are presented in Table 3. The experimental data on the boiling points of alcohols listed in Table 3 are taken from Beilstein [4].

The data of Table 3 show that the theoretically calculated boiling points of alcohols practically completely agree with those found experimentally. Thus, they fully confirm the applicability of the formula (I) suggested by us for accurate calculation of the boiling points of alcohols.

Significant deviations were obtained only for a small number of compounds of a single structural type, especially for alcohols with methyl groups at a maximum of closeness to the hydroxyl, i.e., for such compounds as 2,2,4-trimethylhexanol-3, 2,2,4,4-tetramethylpentanol-3, 2,2,4,4-tetramethylhexanol-3, etc. In these compounds the hydroxyl group is surrounded by methyl groups, and the very fact that only these compounds deviate from the theory serves to indicate the special position of the hydroxyl group in these compounds, which is observed as the result of our method of investigation.

The fact that these compounds have boiling points above the calculated values, it appears to us, can be explained by the decrease in mobility of the methyl groups surrounding the hydroxyl, a decrease which helps produce an

TABLE 3

Boiling Points of Monohydric Alcohols of the Methane Series

Name of alcohol	Boiling point	
	Experimental	Calculated
Isopropyl alcohol	82.5°	80.0°
Isobutyl secondary	100.0	100.0
Isobutyl primary	108	108
Butyl tertiary	82-83	84
Pentanol-2	119	120
Pentanol-3	115-116	116
2-Methylbutanol-1	128-129	129
2-Methylbutanol-2	102	104
2-Methylbutanol-3	111.5	110
2-Methylbutanol-4	130	130
Hexanol-2	139	139
Hexanol-3	135	136
2-Methylpentanol-1	146-148	147
2-Methylpentanol-2	122-123	123
2-Methylpentanol-3	126	126
2-Methylpentanol-4	130-132;135-137	137
2-Methylpentanol-5	151-152; 160-165	151
3-Methylpentanol-1	151-152	149
3-Methylpentanol-2	134 (corrected)	129
3-Methylpentanol-3	122-123	123
2,2-Dimethylbutanol-1	135	137
2,2-Dimethylbutanol-3	119-120	121
2,3-Dimethylbutanol-1	144	144
2,3-Dimethylbutanol-2	120-126	121
Heptanol-2	158-160	160
Heptanol-3	156-157	155
Heptanol-4	154-155	155
2-Methylhexanol-1	162-164	166
2-Methylhexanol-3	141-142	142
2-Methylhexanol-4	145-146	145
2-Methylhexanol-5	147-148	147
2-Methylhexanol-6	148-150	152
2-Methylhexanol-3	170-175	170
2-Methylhexanol-4	139-141	142
3-Methylhexanol-3	149-150	145
2,2-Dimethylpentanol-3	132.5	133
2,3-Dimethylpentanol-2	130.5	137
2,3-Dimethylpentanol-3	122-124;138-140	137
2,3-Dimethylpentanol-4	149-150	145
2,4-Dimethylpentanol-2	133	134
2,4-Dimethylpentanol-3	130-133; 140	135
2,2,3-Trimethylbutanol-3	131-132	132
Octanol-2	178.5	176
Octanol-3	176-178	173
2-Methylheptanol-2	160-162	160
2-Methylheptanol-3	153-154; 162	163
2-Methylheptanol-4	167-168; 164	165
2-Methylheptanol-5	165-166	170
2-Methylheptanol-6	112	170
2-Methylheptanol-7	188	188
3-Methylheptanol-1	181	186

TABLE 3 (Continued)

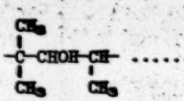
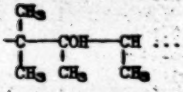
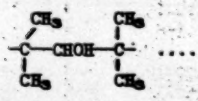
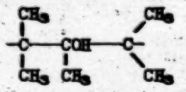
Name of alcohol	Boiling point	
	Experimental	Calculated
3-Methylheptanol-3	161-162°	160°
3-Methylheptanol-5	167-168	165
3-Methylheptanol-6	167-169°	170
4-Methylheptanol-2	168	170
4-Methylheptanol-3	–	163
4-Methylheptanol-4	159-161	160
2,4-Dimethylhexanol-2	150-152	152
2,2-Dimethylhexanol-3	155-157	153
2,3-Dimethylhexanol-2	150-151	156
2,3-Dimethylhexanol-3	158	155
2,4-Dimethylhexanol-4	151-153	152
2,5-Dimethylhexanol-1	179-180	178
2,5-Dimethylhexanol-2	152-154	154
2,5-Dimethylhexanol-3	156; 160-163	155
2,2,3-Trimethylpentanol-3	149-152	150
2,2,4-Trimethylpentanol-4	146-147	154
Nonanol-2	193-195	195
Nonanol-3	194-195	192
Nonanol-4	193	192
Nonanol-5	193	192
2-Methyloctanol-2	178	179
2-Methyloctanol-3	184	182
2-Methyloctanol-4	184	184
2-Methyloctanol-5	184-186	186
2,3-Dimethylheptanol-6	191-192	188
2,4-Dimethylheptanol-4	170-171	171
2,4-Dimethylheptanol-6	194.5	181
2,5-Dimethylheptanol-5	175	173
2,6-Dimethylheptanol-2	172-174	173
2,6-Dimethylheptanol-3	175	176
2,6-Dimethylheptanol-4	172-174	176
2,3,5-Trimethylhexanol-2	171	168
3,3,4-Trimethylhexanol-4	165-166	169
Decanol-2	210	213
Decanol-3	213	210
Decanol-4	210-211	210
2-Methylnonanol-1	222	221
2-Methylnonanol-3	200	201
2,5-Dimethyloctanol-5	192	191
2,6-Dimethyloctanol-8	212-213	213
2,7-Dimethyloctanol-3	193-194	192
3,6-Dimethyloctanol-3	192	191
2,3,6-Trimethylheptanol-6	192-193	190
2,4,6-Trimethylheptanol-4	180-182	183
2,2,5,5-Tetramethylhexanol-3	173-174	174

increase in the degree of association of the alcohol molecules.

In this connection, it is necessary to introduce a special correction for those alcohols in which a maximal concentration of methyl groups is observed surrounding the hydroxyl.

For these alcohols, it is necessary to introduce into the calculation of

the boiling point corrections for the following structural groups:

	Increases in boiling point
	8°
	12
	16
	24

These corrected coefficients are reflected in the degree by which the association of the alcohols is increased when the hydroxyl group is surrounded by methyl groups. Using these supplementary coefficients, we carried through the calculations of boiling point for alcohols with this structure. Our results are listed in Table 4. The experimental data on boiling points, listed in Table 4, are taken chiefly from the work of I. Nazarov [6].

TABLE 4

Boiling Ppints of Alcohols with Methyl Groups Close to the Hydroxyl

Name of alcohol	Boiling point	
	Experimental	Calculated
2,2,4-Trimethylpentanol-3	150-151°	151°
2,2,4-Trimethylhexanol-3	169	170
2,4,4-Trimethylhexanol-3	170-171	170
2,2,4,4-Tetramethylpentanol-3	165-176	168
2,2,4,4-Tetramethylhexanol-3	187	186
2,2,3,4-Tetramethylhexanol-3	190-193	194
3,3,4,5-Tetramethylhexanol-4	197-198	194
2,2,3,4-Tetramethylheptanol-3	212-215	213
2,2,3,4,5-Pentamethylhexanol-3	207-210	209
2,2,3,4,4-Pentamethylhexanol-3	219-222	219
3,3,4,5,5-Pentamethylhexanol-4	243-246	237
2,2,3,4,4-Pentamethylpentanol-3	233-235	237
2,2,3,4,4,5-Hexamethylhexanol-3	235-238	239

Thus it was possible to calculate with a very high degree of accuracy the boiling points of alcohols with the most varied structures.

This makes it possible for us to deduce from the results of our investigation of the boiling points of alcohols, the following five empirical rules:

I. Among isomeric compounds, the primary alcohols boil higher than the secondary, and the secondary higher than the tertiary. But at the same time there are certain cases in which various tertiary alcohols boil higher

than certain secondary alcohols isomeric with them.

2. Of the isomeric alcohols having unbranched hydrocarbon chains, the primary alcohols have the highest boiling point; among the secondary alcohols, those isomers in which the hydroxyl group is attached to the second carbon atom have the highest boiling point.

3. Of those isomeric alcohols which have a single methyl group as a substituent, the first maintains its value according to the rule. But the lowest boiling point among the isomeric primary alcohols will belong to the isomers in which the methyl group is attached to a carbon neighboring the carbon with the hydroxyl group.

Among the secondary alcohols, the highest boiling point will belong to the isomers in which the hydroxyl group is on the second carbon and the methyl group is furthest away from the hydroxyl carbon; the lowest boiling point will belong to the isomers with the hydroxyl upon the 3 and 4 carbons, and a methyl group upon the neighboring carbon atom. The boiling points of isomeric tertiary alcohols are practically identical.

4. Among the isomeric alcohols having two methyl groups as substituents, two cases are possible.

a) Where methyl groups are upon a single carbon, in this case the lowest boiling point among the isomeric primary alcohols will belong to those isomers in which the methyl groups are upon the carbon atom next to the carbon with the hydroxyl. Among the isomeric secondary alcohols, the highest boiling point will belong to the isomers in which the hydroxyl group is upon the second carbon, and the methyl groups are at the greatest distance from the hydroxyl. The lowest boiling point will belong to those isomers among the secondary alcohols in which the hydroxyl group is upon the third or fourth carbon, and the methyl groups upon a neighboring carbon.

b) Where methyl groups are attached to different carbon atoms, the lowest boiling point among the primary alcohols will belong to the isomers in which one methyl group is in position two and the other in position four. The highest boiling point will belong to those isomers of the primary alcohols in which the methyl groups are furthest from the hydroxyl and are upon neighboring carbon atoms. Among the secondary alcohols, the highest boiling point will belong to the isomers in which the hydroxyl group is attached to the second carbon and the methyl groups to the carbons furthest from the hydroxyl, and to the degree in which they are upon neighboring carbon atoms. The lowest boiling point among the isomers of the secondary alcohols will belong to those isomers in which the hydroxyl group is upon carbon atom 3 or 4 and the methyl groups upon atoms 2 and 4, or 3 and 5. Among the isomers of the tertiary alcohols, the boiling points are extremely close to each other.

5. Among the isomeric alcohols in which there are three or more methyl groups as substituents, the rules for the change of boiling point for different isomers can be determined by means of the coefficients previously proposed for combinations of structural groups.

We are sufficiently certain of the correctness of our method to consider it possible to utilize the formula we have proposed for the correction of erroneously determined boiling points in the alcohol series. Thus, we consider that the boiling points of 2-methylpentanol-4, given as 130-132°, of 2-methylpentanol-5 160-165°, of 2,3,-dimethylpentanol-3, 122-124°, of 2-methylheptanol-3, 153-154°, of 2,4-dimethylheptanol-6, 194-195°, etc., are incorrect. Their correct boiling points correspond to those calculated by means of our formula.

Our formula can also be utilized for the calculation of the boiling points

of compounds not yet synthesized. This may be of interest to investigators working on the synthesis of alcohols. Thus, for example, the boiling point of 2,3,-dimethylheptanol-3 should equal 184°, that of 3,4-dimethylhexanol-3 155°, that of 3,4-dimethylhexanol-1 175°, etc.

3. Boiling Points of Ethers

The ethers are the most important derivatives of the alcohols. They serve not only to characterize the latter, but some have already found practical application. An investigation of the data given in the reference books convinces us that the physical chemical properties of the ethers in general and of their boiling points have been experimentally and theoretically studied for very few alcohols. This follows from the fact that ethers have not even been prepared from many very well known alcohols.

In this connection it becomes necessary to make a theoretical study of their physical chemical properties, with the object of understanding the rules according to which these change, and of utilizing these rules for the prediction of properties of not yet synthesized compounds. In our present work, we made it our object to investigate the boiling points of the ethers, using for this purpose the hypotheses we proposed on the basis of our study of the boiling points of alcohols.

As a basis for our investigation, we assumed that the boiling points of ethers with an iso structure could be determined according to formula (I), in accordance with which the boiling point of any isomer can be determined from the boiling point of the compound of normal structure by the use of a number of coefficients.

Therefore, we first determined the general rules of change of the boiling points of methyl and ethyl ethers of the primary alcohols of normal structure. The boiling points of the latter were taken by us as the basis for a study of the boiling points of the ethers with an iso structure. The data on boiling points for ethers with normal structure were taken from Beilstein [5] and are shown in Table 5.

TABLE 5

Boiling Points of Ethers of Normal Structure

Name of alcohol	B.p. of alcohol	B.p. of methyl ether	Difference in b.p. of alcohol and ether	Homologous difference	B.p. of ethyl ether	Difference in b.p. of alcohol and ether	Homologous difference
Methyl	65°	-23.6°	88°	–	10.8°	54°	–
Ethyl	78	11	67	34°	35	43	24°
n-Propyl	98	39	59	23	63	35	28
n-Butyl	118	71	46	32	91	27	28
n-Amyl	138	99	39	28	117°	21	26
n-Hexyl	157	124°	33	25	141°	16	24
n-Heptyl	176	149	27	25	166	10	25
n-Octyl	194	173	21	24	189	5.0	23
n-Nonyl	213	190°	17	23	212°	1.0	23
n-Decyl	231	218°	13	23	234	+ 3.0	23

From the data in Table 5 we can draw the following conclusions:

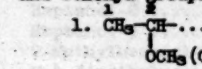
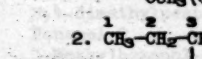
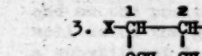
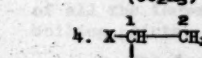
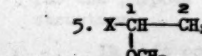
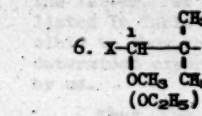
1. From methyl to decyl alcohol, the boiling points of the ethers are considerably lower than the boiling points of the alcohols from which they are obtained. But, as a rule, upon going from methyl alcohol to decyl, the difference

° B.p. computed by us.

between the boiling points of alcohols and of ethers decreases considerably.

2. The homologous difference in boiling points in the series of methyl and ethyl ethers first decreases, and then becomes practically constant. Utilizing this rule, we calculated the boiling points of several unsynthesized ethers. Then we determined the coefficients of the influence of structural factors on boiling point in the series of ethers. The values of the coefficients determined for combinations of structural groups are listed in Table 6, where X is the hydrogen atom or a radical of normal structure. In the series of ethers, the coefficient for the mutual influence of methyl groups retains its value in those cases where the groups are to be found as substituents upon neighboring carbon atoms.

TABLE 6

Structural factor	Correction in boiling point of ether derivative of alcohol of normal structure
In relationship to position of methoxyl and ethoxyl groups in carbon chain:	Lowering of boiling point
1. 	10°
2. 	10°
and further without change.	
In relationship to position of methyl group with respect to methoxyl and ethoxyl:	
3. 	11°
4. 	8
5. 	6
6. 	18°

This coefficient equals +5.0°.

Then, utilizing the coefficients obtained in formula (I), calculations were made of the boiling points of the methyl and ethyl ethers with iso structure. The results obtained by us are listed in Table 7. The experimental data on the boiling points of ethers listed in Table 7 were taken from Beilstein [5].

TABLE 7

Boiling Points of Methyl and Ethyl Ethers from Alcohols with Iso Structure

Name of alcohol	Methyl ether		Ethyl ether	
	Boiling point			
	Experimental	Computed	Experimental	Computed
Isopropyl	32.5°	29.0°	54.0°	53.0°
Primary Isobutyl	58.0	60.0	79.0	80.0
Secondary Isobutyl	–	61.0	–	81.0
Tertiary Isobutyl	53.5	53.0	67-68	73.0
2-Methylbutanol-1	88.0	88.0	108.0	106.0
3-Methylbutanol-1	91.0	91.0	112.0	109.0
2-Methylbutanol-2	–	81.0	102-103	99.0
Hexanol-2	–	114.0	–	131.0
Hexanol-3	–	114.0	–	131.0
2-Methylpentanol-4	–	106.0	121.0	123.0
2-Methylpentanol-5	–	116.0	137.0	133.0
Heptanol-2	–	139.0	–	156.0
Heptanol-3	–	139.0	151.0	156.0
2-Methylhexanol-5	–	131.0	139-142	148.0
2,4-dimethylpentanol-2	–	123.0	140.0	140.0
Nonanol-2	188-189	186.0	200.0	202.0
3-Methylhexanol-4	–	128.0	–	145.0
2-Methylhexanol-3	–	121.0	–	148.0

From the data of Table 7 we can draw the following conclusions.

1. The boiling points of ethers depend on the structure of the molecule and on the position of the methoxyl or ethoxyl group in the carbon chain, as well as on the group's position relative to the methyl group which appears as a substituent in the chain. For the series of ethers we may deduce empirical rules very much analogous to the rules proposed for the alcohols. Here too, of all the isomeric compounds, the ethers of tertiary alcohols have the lowest boiling points.

2. The factual material accumulated by present-day chemistry fully confirms the applicability of the formulas and the coefficients suggested by us for the purpose of accurately calculating the boiling points of ethers of iso structure.

In this connection, they can be utilized for the calculation of boiling points of still unsynthesized ethers on the basis of the structural formulas of the latter. We consider that the boiling points of ethers calculated by us and listed in Table 7 correspond to the actual values. At the same time, it is possible to show that the boiling point of the ethyl ether of 2-methylhexanol-5 determined experimentally is very inaccurate, and should equal that calculated by us.

Thus, the method proposed by us for the investigation of the boiling points of alcohols and ethers makes it possible to reveal a number of very interesting regularities in the change of boiling point in these series of compounds.

SUMMARY

1. A new method has been proposed for the investigation of the boiling points of monohydric alcohols and their ethers. This method makes it possible to determine a number of regularities in the change of boiling point of these compounds.

2. A new formula has been proposed for the calculation of the boiling points of alcohols and ethers. Its applicability is confirmed by the great amount of factual material of present-day chemistry.

3. The quantitative relationship between boiling point and the molecular structure of alcohols and ethers has been determined.

4. The boiling points of a number of still unsynthesized monohydric alcohols and their ethers have been predicted.

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ANESTHETICS OF THE NAPHTHALENE SERIES

V. ESTERS AND ALKYLAMINOALKYLAMIDES OF β-(5-AMINONAPHTHYL-1)-ACRYLIC ACID

S. I. Sergievskaya and K. V. Levshina

The Sergei Ordzhonikidze

All-Union Scientific-Research Chemico-Pharmaceutical Institute. Moscow

The object of the present work was the synthesis of several alkamino esters and dialkylaminoalkylamides of β-(5-aminonaphthyl-1)-acrylic acid, which were of interest to us as anesthetics. For the preparation of these compounds β-(5-nitronaphthyl-1)acrylic acid was needed. This acid is not described in the literature and we decided to obtain it from 5-nitro-1-naphthaldehyde either by means of the Perkin reaction or by the condensation of nitronaphthaldehyde with malonic acid.

According to the data of P. Ruggli and E. Burckhardt [1], 5-nitro-1-naphthaldehyde is formed along with 8-nitro-1-naphthaldehyde by the nitration of 1-naphthaldehyde. For the separation of the isomeric nitroaldehydes, the different solubilities of their anils were utilized, and the yield of 5-nitro-1-naphthaldehyde was not accurately determined.

Upon repeating the nitration of 1-naphthaldehyde and accurately separating the isomers in accordance with the data in the literature, we determined that the yield of 8-nitro-1-naphthaldehyde ammounted to from 18 to 20% of theory, while the yield of 5-nitro-1-naphthaldehyde did not exceed 5%. We noted that the yield of the mixture of nitronaphthaldehydes directly after nitration was completely satisfactory, and therefore it seemed worthwhile first of all to change the method of separation of the nitroaldehydes.

We noted that during the nitration, after half the total amount of 1-naphthaldehyde had been added to the nitric acid, a voluminous crystalline precipitate began to separate. Investigation both of the precipitate and of the acid layer remaining after its separation showed that the separated crystals consisted almost exclusively of 5-nitro-1-naphthaldehyde, while the acid layer contained chiefly 8-nitro-1-naphthaldehyde. The greatest amount of separation of the 5-nitro-1-naphthaldehyde was obtained when nitric acid was used for nitration in the amount theoretically necessary for the introduction of a single nitro group into the naphthaldehyde molecule. With this method of carrying out the reaction, the separation of the isomers took place during the process of nitration itself. One or two recrystallizations from pyridine sufficed for the purification of the separated 5-nitro-1-naphthaldehyde, and its yield amounted to 25%. The 8-nitro-1-naphthaldehyde was separated from the acid mother liquor by the usual method (cf. experimental section) and its yield amounted to 18%. In addition, it was possible to separate the nitronaphthaldehydes with almost the same results by utilizing their different solubilities in pyridine. In this case, the nitration and separation of the mixtures of nitroaldehydes was carried out by the method

indicated in the literature (loc. cit.) and the separation of the isomers was carried out by recrystallizing the mixture from pyridine.

When we utilized the Perkin reaction, β-(5-nitronaphthyl-1)-acrylic acid was obtained in very small yield.

Incomparably better results were obtained by the condensation of 5-nitro-1-naphthaldehyde with malonic acid. By means of this reaction, β-(5-nitronaphthyl-1)-acrylic acid could be obtained either in two steps – first the separation of 5-nitro-1-naphthalmalonic acid, then its decarboxylation – or in a single step, by heating the mixtureof 5-nitro-1-naphthaldehyde with malonic acid in pyridine, during which process condensation and decarboxylation proceeded simultaneously. From β-(5-nitronaphthyl-1)-acrylic acid we obtained by the usual methods its simplest derivatives, several alkylamino esters, and the γ-dimethylamino-α-methylpropylamid:

$$[O_2N-C_{10}H_6-CH=CH-CONH-\underset{\displaystyle CH_3}{\underset{|}{CH}}-(CH_2)_2N(CH_3)_2]$$

as well as the δ-diethylamino-α-methylbutylamid

$$[O_2N-C_{10}H_6-CH=CH-CONH-\overset{\displaystyle CH_3}{\overset{/}{CH}}(CH_2)_3N(C_2H_5)_2],$$

This simple method for the production of β-(5-nitronaphthyl-1)-acrylic acid was shown to be applicable also under other conditions. Earlier, S.I.Sergievskaya and A.S.Elina [2], during the nitration of β-(naphthyl-1)-acrylic acid had isolated as byproducts of the reaction a nitro acid whose structure was not determined, and called by the authors β-(x-nitronaphthyl-1)-acrylic acid. A comparison of the melting points of x-nitro-1-naphthylacrylic acid and 5-nitro-1-naphthylacrylic acid and of their ethyl ethers* showed that these compounds were identical and thus, the question of the structure of the x-nitro-1-naphthylacrylic acid could be considered solved.

By the reduction of the nitro group in the above mentioned alkamino ethers and alkylamides of β-(5-nitronaphthyl-1)-acrylic acid by the use of iron and hydrochloric acid in alcoholic solution we obtained the corresponding compound β-(5-aminonaphthyl-1)-acrylic acid. We also attempted to utilize the interesting discovery of E. Blout and D. Silverman [3] of the possibility of catalytic reduction of the nitro group alone in the alkyl ethers of nitrocinnamic acid, without saturating the unsaturated aliphatic bond, and carried out several reduction experiments by the same method with the alkamino esters of 5-nitro-1-naphthylacrylic acid; however, we obtained either products with incompletely reduced nitro groups or alkamino esters of β-(5-aminonaphthyl-1)-propionic acid.

The anesthetic properties of the alkamino esters and amides of β-(5-aminonaphthyl-1)-acrylic acid were tested on the corneas of rabbits. The tests were carried out in the pharmacological department of the All-Union Scientific Research Chemico-Pharmaceutical Institute with the aid of scientific coworker Yu.I.Syrneva. The amides did not produce complete anesthesia; the dimethylamino- and diethylamino-ethyl esters had comparatively weak anesthetic properties and resulted in tearing of the eyes and hyperemia. The diethylaminopropyl ester had considerably better pharmacological properties. These observations showed to what degree the position of the amino group in the naphthalene ring influenced the pharmacological properties of compounds of this type, and also showed, in accordance with a previous communication (Sergievskaya and Elina [2]) that the distinctive characteristics of the corresponding esters of β-(4-amino-1)-naphthyl-

*m.p. of β-(x-nitronaphthyl-1)-acrylic acid 254°; m.p. of β-(5-nitronaphthyl-1)-acrylic acid 257-259°; m.p. of the ethyl ether of β-(x-nitronaphthyl-1)-acrylic acid 105°; m.p. of the ethyl ether of β-(5-nitronaphthyl-1)-acrylic acid 104-105°.

acrylic acid led more quickly to the production of anesthesia, permitted it to continue longer, and did not result in any side effects.

EXPERIMENTAL

5-Nitro-1-naphthaldehyde and 8-Nitro-1-naphthaldehyde

1. In a three-necked round-bottomed flask, fitted with a stirrer, a thermometer, and a dropping funnel, there was placed 50 ml of nitric acid (sp. gr. 1.47), which was cooled to a temperature of -5°. Then, with mechanical stirring, there was gradually added 10 g of 1-naphthaldehyde at a rate sufficiently slow so that the temperature of the mixture did not rise above 0°. After all the 1-naphthaldehyde had been added, the reaction mixture was stirred for 30 minutes more with cooling, and then until room temperature was reached. The nitro compounds, which had separated during the reaction in the form of yellow crystalline substances, were filtered off on a Schott filter and washed first with concentrated and then with dilute nitric acid, and after that with cold water. They were then dried and recrystallized from five times their weight of pyridine. After one or two recrystallizations from pyridine* the 5-nitro-1-naphthaldehyde melted at 136-137°. It was in the form of shining light yellow crystals shaped like small needles, very soluble in pyridine upon heating and in ethyl acetate, somewhat less soluble in methyl alcohol. There was obtained 3.24 g of 5-nitro-1-naphthaldehyde, which amounted to 25% of the theoretical, calculated on the basis of the 1-naphthoic aldehyde.

The acid solution obtained by filtering off on a Schott filter the precipitate formed in the process of nitration was then carefully poured on ice. A yellow oily powder was obtained. After drying in a desiccator, this had a melting point of 85-100°. After numerous recrystallizations from ethyl acetate, 1.8 g of 8-nitro-1-naphthaldehyde was obtained in the form of yellow crystals with m.p. 123-124°. From the pyridine mother liquors remaining after precipitation of the 5-nitro isomer, an additional 0.8 g of 8-nitro-1-naphthaldehyde with m.p. 122-123° was obtained. The total of 8-nitro-1-naphthaldehyde obtained was 2.3 g, which amounted to 17.8% of the theoretical amount, basing the calculations on 1-naphthoic aldehyde.

2. In a three-necked flask fitted with a stirrer, a thermometer, and a dropping funnel there was placed 100 ml of nitric acid (sp. gr. 1.47); this was cooled to a temperature of -5°. Then there was gradually added with mechanical stirring 10 g of 1-naphthoic aldehyde, at a speed that did not permit the temperature of the reaction mixture to rise above 0°. When all the 1-naphthoic aldehyde had been added, stirring was continued for 30 minutes more with cooling, and then without cooling until room temperature was reached. Then the reaction mixture was poured on ice. The yellow material which separated out was filtered off with suction and washed on the filter with water and a small amount of ethyl acetate. M.p. 100 to 110°. The mixture of nitro compounds obtained (10.4 g) was crystallized from pyridine. The 5-nitronaphthoic aldehyde was obtained with a m.p. of 136-137°. The yield was 20% of the theoretical, based on the 1-naphthoic aldehyde used. Approximately $^2/_3$ of the pyridine was distilled off from the mother liquor, and a dark yellow substance separated, from which, after numerous recrystallizations from ethyl acetate, there was obtained 8-nitro-1-naphthaldehyde with m.p. 123-124°. The yield was 22.1% of the theoretical, basing the calculation on the 1-naphthoic aldehyde used.

5-Nitro-1-naphthalmalonic acid. In a three-necked round-bottomed flask of 50 ml capacity, fitted with a stirrer, a thermometer and a reflux condenser, there

*Upon standing there separated from the pyridine mother liquors the following fractions of crystalline substances: first one with m.p. 110-115°, then one with m.p. 95-100°. These portions were combined and recrystallized several times from ethyl acetate to which animal charcoal had been added. The product obtained had m.p. 123-124°.

were placed 4 g of 5-nitro-1-aldehyde, 4 g of malonic acid, and 10 ml of glacial acetic acid. The mixture was heated on the water bath at a temperature of 85-90° with continuous stirring for 12 hours. The acid formed during the reaction separated out toward the end of the stirring in the form of a yellow precipitate, which was filtered off and washed with a small amount of chloroform. The filtrate was concentrated to give an additional quantity of the acid. After recrystallization from 70% acetic acid, 3.9 g of 5-nitro-1-naphthalmalonic acid was obtained in the form of white crystals with m.p. 250-252°.

3.011 mg substance: 6.460 mg CO_2; 0.866 mg H_2O.
3.030 mg substance: 6.508 mg CO_2; 0.840 mg H_2O.
6.195 mg substance: 0.260 ml N_2 (20.5°, 737 mm).
Found %: C 58.51, 58.57; H 3.21, 3.10; N 4.72.
$C_{14}H_9O_8N$. Computed %: C 58.53; H 3.14; N 4.87.

β-(5-nitronaphthyl-1)-acrylic acid. 1) The decarboxylation of 5-nitro-1-naphthalmalonic acid

a) In a round-bottomed flask with a reflux air condenser there was placed 2 g of 5-nitro-1-naphthalmalonic acid. This was heated on an oil bath at a temperature of 260° for four hours (until no more carbon dioxide was evolved). The β-(5-nitronaphthyl-1)-acrylic acid formed was dissolved in a hot 10% solution of soda and the solution was boiled with activated carbon, then filtered, and precipitated by the addition of dilute hydrochloric acid. The precipitate was colorless. There was obtained 1.4 g of β-(5-nitronaphthyl-1)-acrylic acid, with m.p. 256-257°; the acid was very difficultly soluble in chloroform, ether, and benzene, and somewhat better soluble in alcohol, glacial acetic acid, acetone, and ethyl acetate.

b) 0.8 g of 5-nitronaphthalmalonic acid and 8 ml of pyridine were placed in a round-bottomed flask with a reflux condenser and heated on a glycerine bath for 3 hours, then half the amount of pyridine was driven off in vacuum, and the precipitate which formed was filtered off and recrystallized from alcohol. There was obtained 0.6 g of β-(5-nitronaphthyl-1)-acrylic acid, with m.p. 257-258°.

3.362 mg substance: 7.922 mg CO_2; 1.142 mg H_2O.
3.270 mg substance: 7.690 mg CO_2; 1.090 mg H_2O.
7.840 mg substance: 0.397 ml N_2 (25°, 736 mm).
7.900 mg substance: 0.410 ml N_2 (25°, 736 mm).
Found %: C 64.26, 64.14; H 3.80, 3.79; N 5.61, 5.75.
$C_{13}H_9O_4N$. Computed %: C 64.17; H 3.73; N 5.76.

2) The condensation of 5-nitro-1-naphthoic aldehyde with malonic acid in the presence of pyridine. In a round-bottomed flask with a reflux condenser there were placed 2.2 g of 5-nitro-1-naphthaldehyde, 3 g of malonic acid, and 6 ml of pyridine. The mixture was heated on the boiling water bath for 2 hours (until there were no more bubbles formed on the surface of the reaction mixture). Then the contents of the flask were boiled for 5 to 7 minutes more on a gauze over a weak flame. Part of the pyridine was then driven off in vacuum, and the precipitate which settled out on cooling was filtered off and recrystallized from alcohol. There was obtained 1.9 g of β-(5-nitronaphthyl-1)-acrylic acid in the form of a colorless precipitate with m.p. 257-258.5°.

4.118 mg substance: 9.696 mg CO_2; 1.364 mg H_2O.
3.239 mg substance: 7.620 mg CO_2; 1.090 mg H_2O.
6.510 mg substance: 0.329 ml N_2 (13°, 745 mm).
6.730 mg substance: 0.338 ml N_2 (13°, 745 mm).
Found %: C 64.21, 64.16; H 3.71, 3.77; N 5.84, 5.87.
$C_{13}H_9O_4N$. Computed %: C 64.17; H 3.73; N 5.76.

3) The Perkin Reaction of 5-nitro-1-naphthaldehyde. 3 g of anhydrous freshly fused sodium acetate and 9 g of acetic anhydride were placed in a small round-bottomed flask with a reflux condenser and heated on an oil bath at a temperature of 137-140° for 6 hours. The reaction mixture, which solidified upon cooling, was diluted with 60 ml of water, and a 25% solution of caustic soda was gradually added while the mixture was heated on the water bath until there was no more odor of acetic anhydride. The solution was filtered to remove the insoluble precipitate, and the β-(5-nitronaphthyl-1)-acrylic acid was precipitated from the filtrate by the addition of dilute (1:1) hydrochloric acid. It came down as a dark amorphous precipitate. After numerous recrystallizations from alcohol, a very small quantity of the compound was obtained with m.p. 256-257°.

3.935 mg substance: 9.305 mg CO_2; 1.385 mg H_2O.
2.900 mg substance: 6.829 mg CO_2; 0.998 mg H_2O.
8.020 mg substance: 0.392 ml N_2 (16°, 744 mm).
Found %: C 64.49, 64.22; H 3.93, 3.85; N 5.65.
$C_{13}H_9O_4N$. Computed %: C 64.17; H 3.73; N 5.76.

The acid chloride of β-(5-nitronaphthyl-1)-acrylic acid. 1.5 g of β-(5-nitronaphthyl-1)-acrylic acid and 4 g of thionyl chloride were placed in a round-bottomed flask, fitted with a reflux condenser to which a calcium chloride tube was attached, heated on the water bath for 6 hours at a bath temperature of 80°. The thionyl chloride was then driven off in vacuum, and the remaining yellow crystalline mass was quickly recrystallized twice from absolute benzene. There was obtained 1.1 g of the acid chloride of β-(5-nitronaphthyl-1)-acrylic acid, in the form of yellow crystals with a m.p. of 132-133.5°, fairly well soluble in benzene and chloroform upon heating. The acid chloride was very unstable, and upon standing in air quickly decomposed with the formation of the original acid.

0.3150 g substance: 12.11 ml 0.1 N $AgNO_3$.
Found %: Cl 13.52.
$C_{13}H_8O_3NCl$. Computed %: Cl 13.55.

The amide of β-(5-nitronaphthyl-1)-acrylic acid. In a small flask of 20 ml capacity there were placed 0.5 g of the acid chloride of β-(5-nitronaphthyl-1)-acrylic acid and 8 ml of a 26% aqueous solution of ammonia. The mixture was carefully stirred for several minutes. The light yellow precipitate formed was filtered off, washed with water, dried, and recrystallized twice from 96% ethyl alcohol. There was obtained 0.37 g of the amide of β-(5-nitronaphthyl-1)-acrylic acid in the form of light yellow crystals, fairly well soluble in ethyl alcohol and acetone, with m.p. 227-228.5°.

4.400 mg substance: 0.451 ml N_2 (22°, 734 mm).
3.335 mg substance: 0.348 ml N_2 (22°, 734 mm).
Found %: N 11.46, 11.66.
$C_{13}H_{10}O_3N_2$. Computed %: N 11.57.

The methyl ester of β-(5-nitronaphthyl-1)-acrylic acid. In a round-bottomed flask to which was attached a reflux condenser, there were placed 2 g of β-(5-nitronaphthyl-1)-acrylic acid, 100 ml of absolute methyl alcohol, and 0.6 ml of concentrated sulfuric acid (sp. gr. 1.84). The mixture was heated on the water bath for 8 hours. The excess of alcohol was then driven off, and the residue was diluted first with water, then with a 10% solution of soda until there was an alkaline reaction to litmus. The methyl ester was extracted with ether, and the ether solution washed several times with water, then dried over roasted sodium sulfate. The ether was driven off, and the crystalline mass remaining was recrystallized from methyl alcohol. There was obtained 1.5 g of the methyl ester of β-(5-nitronaphthyl-1)-acrylic acid, as lustrous clear yellow crystals

with m.p. 120-121°, well soluble in ether in the cold and in alcohol upon heating.

7.343 mg substance: 0.364 ml N_2 (21.5°, 728.2 mm).
7.493 mg substance: 0.363 ml N_2 (19.5°, 727.5 mm).
Found %: N 5.48, 5.42.
$C_{14}H_{11}O_4N$. Computed %: N 5.44.

The ethyl ester of β-(5-nitronaphthyl-1)-acrylic acid. 0.7 g of β-(5-nitronaphthyl-1)-acrylic acid, 60 ml of absolute ethyl alcohol, and 0.2 ml of concentrated sulfuric acid (sp. gr. 1.84) were heated on the water bath for 8 hours. After the usual treatment and recrystallization from alcohol, there was obtained 0.65 g of the ethyl ester of β-(5-nitronaphthyl-1)-acrylic acid in the form of light yellow crystals with m.p. 104-105°, well soluble in ether and in chloroform, soluble in alcohol upon heating, and insoluble in water.

4.535 mg substance: 0.210 ml N_2 (22°, 720 mm).
5.905 mg substance: 0.265 ml N_2 (21°, 721 mm).
Found %: N 5.07, 4.97.
$C_{15}H_{13}O_4N$. Computed %: N 5.16.

The cyclohexyl ester of β-(5-nitronaphthyl-1)-acrylic acid. In a round-bottomed flask, 0.8 g of the acid chloride of β-(5-nitronaphthyl-1)-acrylic acid was dissolved in 50 ml of absolute benzene, and to the warm solution there was gradually added with stirring 1.2 g of freshly distilled cyclohexanol. The mixture was heated on the water bath with a reflux condenser at the boiling point of the benzene for 3 hours. The benzene was driven off, and the oily material remaining was dissolved in ether. The ether solution was washed with a 5% solution of soda, then with water, and dried over sodium sulfate. The oily substance remaining after removal of the ether was crystallized from 96% ethyl alcohol. It melted at 85.5-86.5°. The cyclohexyl ester of β-(5-nitronaphthyl-1)-acrylic acid is very soluble in ether, acetone, and alcohol, and soluble with somewhat great difficulty in benzene and chloroform. Yield 0.71 g.

4.400 mg substance: 11.338 mg CO_2; 2.300 mg H_2O.
3.210 mg substance: 8.262 mg CO_2; 1.708 mg H_2O.
4.906 mg substance: 0.198 ml N_2 (27.5°, 741 mm).
5.930 mg substance: 0.226 ml N_2 (20.5°, 745 mm).
Found %: C 70.28, 70.19; H 5.85, 5.95; N 4.47, 4.53.
$C_{19}H_{19}O_4N$. Computed %: C 70.13; H 5.89; N 4.31.

The chloropropyl ester of β-(5-nitronaphthyl-1)-acrylic acid. In a three-necked round-bottomed flask fitted with a mechanical stirrer and a reflux condenser there was placed 100 ml of an alcoholic solution of caustic potash (0.6 g caustic potash) and this was heated on the water bath (bath temperature 60 to 65°) and stirred energetically while 2 g of β-(5-nitronaphthyl-1)-acrylic acid was added. The acid was added in small portions as rapidly as it was transformed into the potassium salt. To the alcoholic solution there was added gradually, with careful stirring, 15 g of chlorobromopropane. The mixture was then stirred for 7 hours more at the boiling point of the alcohol. The potassium bromide formed was then filtered off, and the alcohol driven off from the filtrate in vacuum. The remaining oily substance was heated on the water bath in vacuum for an hour, then dissolved in ether. The ether solution was washed several times with a 10% solution of sodium carbonate, then with water, and dried over calcined sodium sulfate. The ether was driven off, and the remaining oily material was rubbed until crystallization began. Upon standing, it formed oily crystals. By means of crystallization from 96% ethyl alcohol, the chloropropyl ester of β-(5-nitronaphthyl-1)-acrylic acid was obtained in the form of a light yellow crystalline material. The m.p. was 82.5 to 84°. The compound was very soluble in alochol and in ether. Yield 1.35 g.

6.320 mg substance: 0.247 ml N_2 (19.5°, 743 mm).
Found %: N 4.46.
$C_{18}H_{14}O_4NCl$. Computed %: N 4.37.

The ethyl ester of β-(5-acetaminonaphthyl-1)-acrylic acid. In a three-necked round-bottomed flask fitted with a mechanical stirrer and a reflux condenser, there was placed 1.3 g of the ethyl ester of β-(5-nitronaphthyl-1)-acrylic acid, dissolved in 50 ml of 98% ethyl alcohol. The solution was heated on the water bath to 57-60° and 0.2 ml of concentrated hydrochloric acid (sp. gr 1.19) was added. Then, while vigorous stirring was continued for an hour, 1 g of iron filings was added. The stirring was continued for 6 hours more at the boiling point of alcohol. Then the solution was filtered off and the alcohol driven off in vacuum. To the viscous oily material that remained, acetic anhydride was added. There was an immediate formation of a light yellow crystalline material, which was filtered off and recrystallized twice from ethyl alcohol. The ethyl ester of β-(5-acetaminonaphthyl-1)-acrylic acid was in the form of colorless, shining crystals with m.p. 171.5-172°, soluble in alcohol, difficultly soluble in ether. Yield 0.4 g.

4.310 mg substance: 0.189 ml N_2 (18°, 747.5 mm).
Found %: N 5.06.
$C_{17}H_{17}O_3N$. Computed %: N 4.95.

The β-dimethylaminoethyl ester of β-(5-nitronaphthyl-1)-acrylic acid. In a round-bottomed flask there was placed 3 g of the acid chloride of β-(5-nitronaphthyl-1)-acrylic acid, dissolved in 30 ml of absolute benzene. To the warm solution there was gradually added, with stirring, 1.1 g of freshly distilled dimethylaminoethanol. The flask was fitted with a reflux condenser and the mixture heated on the water bath at the boiling point of the solution for 5 hours. The hydrochloride precipitate formed was filtered off (3.2 g) and dissolved in water. The aqueous solution was filtered. The addition to the filtrate of a 10% soda solution precipitated the free alkamino ester base, which was extracted with ether. The ether solution was washed with water, dried over sodium sulfate, and the ether distilled off. The remaining oily material was heated on the water bath in vacuum for an hour to remove traces of the unreacted dimethylaminoethanol. The oily material hardened upon cooling, to give a crystalline mass, which was recrystallized from absolute alcohol. The free base, the β-dimethylaminoethyl ester of β-(5-nitronaphthyl-1)-acrylic acid, was in the form of lustrous light yellow crystals with m.p. 64°, soluble in ether, alcohol, and acetone.

4.479 mg substance; 0.354 ml N_2 (15.5°, 721 mm).
Found %: N 8.89.
$C_{17}H_{18}O_4N_2$. Computed %: N 8.91.

The hydrochloride of the β-dimethylamindethyl ester of β-(5-nitronaphthyl-1)-acrylic acid. 1.1 g of the free β-dimethylaminoethyl ester of β-(5-nitronaphthyl-1)-acrylic acid was dissolved in absolute ether. The ether solution was acidified with hydrogen chloride, which had been dissolved in ether. There precipitated out 1 g of the hydrochloride of the β-dimethylaminoethyl ester of β-(5-nitronaphthyl-1)-acrylic acid. After recrystallization from alcohol, it was obtained in the form of a powdery light yellow material, insoluble in ether, highly soluble in water, and with more difficulty in alcohol, with m.p. 198-199°.

6.930 mg substance: 0.488 ml N_2 (14.5°, 720.5 mm).
Found %: N 7.95.
$C_{17}H_{18}O_4N_2 \cdot HCl$. Computed %: N 7.99.

The hydrochloride of the β-dimethylaminoethyl ester of β-(5-aminonaphthyl-1)-acrylic acid. In a three-necked round-bottomed flask fitted with a stirrer and a

reflux condenser there was placed 2.4 g of the hydrochloride of the β-dimethylamino ester of β-(5-nitronaphthyl-1)-acrylic acid which had been dissolved by heating in 50 ml of 96% ethyl alcohol. The solution of alkamino ester hydrochloride obtained was heated up to 57-60°, and 0.1 ml of concentrated hydrochloric acid (sp. gr. 1.19) was added to it. Then, with vigorous stirring, there was added in the course of an hour 1.5 g of iron filings. The contents of the flask were then stirred for 2 more hours at the boiling point of the alcoholic solution. Upon further standing of the reaction mixture, there separated out yellow crystals of the hydrochloride of the β-dimethylaminoethyl ester of β-(5-aminonaphthyl-1)-acrylic acid, which were filtered off together with the inorganic residue.

The precipitate obtained was boiled repeatedly with ethyl alcohol, and a subsequent filtration was used to separate the hydrochloride of the alkamino ester from the inorganic residue. All the alcoholic solutions of the hydrochloride of the alkamino ester were united and the alcohol was driven off in vacuum until crystallization began. A yellow crystalline precipitate separated out (1.1 g), which after two recrystallizations from ethyl alcohol was in the form of shining yellow crystals, very soluble in water and alcohol, soluble with more difficulty in chloroform, and almost insoluble in ether. The m.p. was 194-194.5°. Dilute aqueous solutions hydrolyzed upon standing.

2.801 mg substance: 0.214 ml N_2 (16.5°, 739.5 mm).
4.015 mg substance: 0.301 ml N_2 (18°, 745 mm).
Found %: N 8.77, 8.62.
$C_{17}H_{20}O_2N_2 \cdot HCl$. Computed %: N 8.74.

The hydrochloride of the β-diethylaminoethyl ester of β-(5-nitronaphthyl-1)-acrylic acid. In a round-bottomed flask there was placed 0.5 g of the acid chloride of β-(5-nitronaphthyl-1)-acrylic acid, dissolved in 15 ml of hot absolute benzene. To the warm solution there was gradually added with stirring 0.25 g of freshly distilled β-diethylaminoethanol. The reaction flask was fitted with a reflux condenser and the mixture heated on the water bath for 3 hours. The hydrochloride formed was filtered off and purified by transformation into the base. For this purpose, the hydrochloride was dissolved in water, the aqueous solution filtered out, and a 10% solution of soda added to the filtrate until the reaction to litmus was alkaline. The base which separated out was extracted with ether. The ether solution was washed with water and dried over sodium sulfate. After removal of the ether, an oily substance remained, which was heated on the boiling water bath in vacuum for 1 hour to remove traces of the unreacted β-dimethylaminoethanol. It was then dissolved in absolute ether and the ether solution cooled with ice. To it was added drop by drop an ether solution of hydrogen chloride until there was a weak acid reaction to Congo Red. There separated out 0.3 g of the hydrochloride of the β-diethylaminoethyl ester of β-(5-nitronaphthyl-1)-acrylic acid, which was recrystallized from 96% ethyl alcohol to give light yellow crystals with m.p. 199-200°, very soluble in water and in glacial acetic acid, soluble in methyl and ethyl alcohols upon heating, almost insoluble in benzene, carbon tetrachloride, and dichloroethane.

5.100 mg substance: 0.324 ml N_2 (12°, 738.5 mm).
4.651 mg substance: 0.296 ml N_2 (12°, 738.5 mm).
Found %: N 7.39, 7.41.
$C_{19}H_{22}O_4N_2 \cdot HCl$. Computed %: N 7.39.

The hydrochloride of the β-diethylaminoethyl ester of β-(5-aminonaphthyl-1)-acrylic acid. In a three-necked round-bottomed flask fitted with a mechanical stirrer and a reflux condenser, there was placed 3.3 g of the hydrochloride of the β-diethylaminoethyl ester of β-(5-nitronaphthyl-1)-acrylic acid, which was dissolved by heating in 60 ml of 98% ethyl alcohol. To the solution there was added 0.15 ml of hydrochloric acid (sp. g. 1.19). Then, with mechanical stirring,

there was added in the course of 1.5 hours 2.2 g of iron filings. The reaction mixture was then stirred for 4 hours more at the boiling point of the solution. Upon cooling, there separated out dark yellow crystals of the β-diethylaminoethyl ester of β-(5-aminonaphthyl-1)-acrylic acid. These were first filtered off along with the inorganic residue and then extracted by means of boiling many times with ethyl alcohol. All the filtrates were combined, and the alcohol driven off in vacuum until the volume of the solution was reduced to one third its initial size. Upon standing, there separated out of the solution an amorphous precipitate of the alkamino ester hydrochloride. The material obtained was purified by transformation into the free base. Upon acidifying the ether solution of the alkamino ester base with an ethereal solution of hydrogen chloride, 2.0 g of the hydrochloride of the β-diethylaminoethyl ester of β-(5-aminonaphthyl-1)-acrylic acid separated out. After recrystallization from ethyl alcohol a yellow powdery material was obtained, with m.p. 193-194°, very soluble in water and in ethyl alcohol, insoluble in ether. The weak aqueous solutions (less than 0.5%) hydrolyzed upon standing.

3.565 mg substance: 0.235 ml N_2 (12.5°, 752 mm).
4.034 mg substance: 0.276 ml N_2 (14.0°, 746.5 mm).
Found %: N 7.80, 8.00.
$C_{19}H_{24}O_2N_2 \cdot HCl$. Computed %: N 8.03.

The hydrochloride of the γ-diethylaminopropyl ester of β-(5-nitronaphthyl-1)-acrylic acid. 0.7 g of caustic potash was dissolved in 100 ml of absolute ethyl alcohol, and the solution was placed in a three-necked round-bottomed flask fitted with a mechanical stirrer and a reflux condenser. To the solution there was gradually added with stirring 2.3 g of β-(5-nitronaphthyl-1)-acrylic acid, and the flask was heated on the water bath at 60 to 65°. To the alcoholic solution of the potassium salt obtained, there was added 3 g of γ-diethylaminopropyl chloride, and the reaction mixture was stirred for 4 hours while the bath temperature was maintained at 80 to 85°. Upon cooling, the potassium chloride was filtered off. The alcohol was driven off from the filtrate and the oily residue was heated on a boiling water bath in vacuum to remove the traces of unreacted γ-diethylaminopropyl chloride. The free alkamino ester obtained was dissolved in ether, the ether solution washed with water, and dried over sodium sulfate. The ether was then driven off in vacuum, and the oily residue was dissolved in absolute ether. The ether solution of alkamino ester thus obtained was cooled with ice, and an ether solution of hydrogen chloride added drop by drop until there was an acid reaction by Congo red. A light yellow precipitate (2.0 g) separated out; this was filtered off and recrystallized from 98% ethyl alcohol. The hydrochloride of the γ-diethylaminopropyl ester of β-(5-nitronaphthyl-1)-acrylic acid was in the form of light yellow crystals with m.p. 214.5-216°, very soluble in water and alcohol and insoluble in ether.

4.705 mg substance; 0.294 ml N_2 (17.0°, 745 mm).
2.684 mg substance: 0.172 ml N_2 (17.0°, 735.5 mm).
Found %: N 7.21, 7.27.
$C_{20}H_{24}O_4N_2 \cdot HCl$. Computed %: N 7.13.

The hydrochloride of the γ-diethylaminopropyl ester of β-(5-aminonaphthyl-1)-acrylic acid. In a three-necked round bottomed flask fitted with a mechanical stirrer and a reflux condenser there were placed 2 g of the hydrochloride of the γ-diethylaminopropyl ester of β-(5-nitronaphthyl-1)-acrylic acid dissolved in 75 ml of 96% ethyl alcohol, and 0.1 ml of hydrochloric acid (sp. gr. 1.19). Then, with heating and vigorous stirring, there was gradually added 1.5 g of iron filings. The experiment was then further carried out and the substance treated in the same manner as in the preceding similar experiments. The crystalline precipitate obtained (1.3 g) was recrystallized several times from ethyl alcohol. The hydrochloride of the γ-diethylaminopropyl ester of β-(5-amino-

naphthyl-1)-acrylic acid was in the form of a yellow powder with m.p. 212-212.5°, very soluble in water, soluble in alcohol, and almost insoluble in ether.

3.126 mg substance: 0.208 ml N_2 (19.5°, 733.5 mm).
2.096 mg substance: 0.138 ml N_2 (21°, 746.5 mm).
Found %: N 7.49, 7.51.
$C_{20}H_{28}O_2N_2 \cdot HCl$. Computed %: N 7.73.

The γ-dimethylamino-α-methylpropylamide of β-(5-nitronaphthyl-1)-acrylic acid. In a three-necked round-bottomed flask fitted with a mechanical stirrer and a reflux condenser there was placed 0.65 g of the acid chloride of β-(5-nitronaphthyl-1)-acrylic acid, dissolved in 50 ml of absolute benzene. To this acid chloride solution there was gradually added with stirring 0.5 g of γ-dimethylamino-α-methylpropylamine. During this addition a rapid heating of the reaction mixture was observed. After the addition was complete, the contents of the flask were stirred for an additional 4 hours while the flask was heated on the water bath at a temperature of 50 to 55°. The benzene was then driven off in vacuum. The residue was dissolved in water, the aqueous solution filtered, and a 10% solution of soda used to precipitate the free basic dialkylaminoalkylamide from the filtrate. This was then extracted with ether. The ether solution was washed with water and dried over sodium sulfate.* Upon subsequent standing, the oily substance hardened. After 1 or 2 recrystallizations from 96% ethyl alcohol, the γ-dimethylamino-α-methylpropylamide of β-(5-nitronaphthyl-1)-acrylic acid was in the form of a yellow powder which melted at 144-145°, dissolved in ether and alcohol, was not so soluble in chloroform, and was barely soluble in carbon tetrachloride. Yield 0.5 g.

2.591 mg substance: 0.273 ml N_2 (20.5°, 750 mm).
3.205 mg substance: 0.351 ml N_2 (24°, 736 mm).
Found %: N 12.10, 12.19.
$C_{19}H_{23}O_3N_3$. Computed %: N 12.02.

The citrate of the γ-dimethylamino-α-methylpropylamide of β-(5-aminonaphthyl-1)-acrylic acid. In a three-necked round-bottomed flask fitted with a mechanical stirrer and a reflux condenser there were placed a solution of 1 g of the γ-dimethylamino-α-methylpropylamide of β-(5-nitrnnaphthyl-1)-acrylic acid in 45 ml of 96% ethyl alcohol and 0.1 ml of concentrated hydrochloric acid. Then, over a period of 1 hour, 0.8 g of iron filings was added. The mixture was stirred for 3 hours at the boiling point of the alcohol. At the end of the reaction, the inorganic residue was filtered off and washed several times on the filter with hot alcohol. All the alcoholic solutions were united and the alcohol driven off in vacuum. The oily residue was dissolved in water. To the aqueous solution there was added a 10% solution of soda until an alkaline reaction was produced and the free basic dialkylaminoalkylamide which separated out was extracted with ether. The ether solution was washed with water and dried over sodium sulfate. The solution was filtered and an alcoholic solution of citric acid was added to precipitate 0.7 g of the citrate in the form of a yellow precipitate which deliquesced in the air. After several reprecipitations from alcoholic solutions by means of absolute ether and repeated washing with absolute ether, the substance was dried in a vacuum desiccator. The citrate of the γ-dimethylamino-α-methylpropylamide of β-(5-aminonaphthyl-1)-acrylic acid was in the form of a yellow amorphous powder, hygroscopic, melting with decomposition at a temperature of 126-128°. It was very soluble in water and alcohol, soluble with difficulty in chloroform, and almost insoluble in ether.

3.126 mg substance: 0.218 ml N_2 (25°, 739.5 mm).
Found %: N 7.77.
$C_{19}H_{25}ON_3 \cdot C_6H_8O_7 \cdot H_2O$. Computed %: N 8.05.

*The ether was driven off and the oily residue heated for an hour in vacuum.

The δ-diethylamino-α-methylbutylamide of β-(5-nitronaphthyl-1)-acrylic acid. For the reaction there were used 0.75 g of the acid chloride of β-(5-nitronaphthyl-1)-acrylic acid, 20 ml of absolute benzene, and 0.5 g of δ-diethylamino-α-methylbutylamine. The reaction was carried out and the amide isolated exactly as in the previous experiment to give the δ-dimethylamino-α-methylpropylamide of 5-nitro-1-naphthylacrylic acid. For purposes of purification, the diethylamino-α-methylbutylamide was transformed into the hydrochloride and then back again into the free base, and the latter allowed to stand a long time in the vacuum desiccator. A yellow powder was obtained with m.p. 120-121°, very soluble in alcohol and acetone, soluble with difficulty in ether. Yield 0.53 g.

2.712 mg substance: 0.267 ml N_2 (20°, 738 mm).
2.493 mg substance: 0.244 ml N_2 (20.5°, 738 mm).
Found %: N 11.13; 11.06.
$C_{22}H_{29}N_3O_3$. Computed %: N 10.97.

The citrate of the δ-diethylamino-α-methylbutylamide of β-(5-aminonaphthyl-1)-acrylic acid. In a three-necked round-bottomed flask fitted with a mechanical stirrer and a reflux condenser there were placed a solution of 1.7 g of the δ-diethylamino-α-methylamide of β-(5-nitronaphthyl-1)-acrylic acid in 50 ml of 96% ethyl alcohol and 0.15 ml of hydrochloric acid (sp. gr. 1.19). Then, while the solution was stirred, there was gradually added over the course of an hour 1.5 g of iron filings. At the end of the addition of the iron filings, the reaction mixture was stirred for 4 hours more at the boiling point of the alcohol. Then the inorganic residue was filtered off and washed several times on the filter with hot alcohol. All the alcoholic solutions were united and the alcohol driven off in vacuum. The hydrochloride of the δ-diethylamino-α-methylbutylamide of β-(5-aminonaphthyl-1)-acrylic acid remained in the form of a viscous oily mass. The hydrochloride was transformed by treatment with a solution of soda into the free base, and to an ether solution of the basic amide there was added an alcoholic solution of citric acid until there was a weakly acid reaction. The citrate of the δ-diethylamino-α-methylbutyl amide of β-(5-aminonaphthyl-1)-acrylic acid precipitated out (1 g). After reprecipitation from absolute alcohol with ether, and repeated washing with absolute ether and drying in a vacuum desiccator, the compound was in the form of a yellow powder, melting with decomposition at a temperature of 133-135°. It was very soluble in water, alcohol, and acetone, and almost insoluble in ether. The citrate was hygroscopic and upon long standing in the air deliquesced.

4.793 mg substance: 0.314 ml N_2 (23°, 736 mm).
Found %: N 7.32.
$C_{22}H_{31}ON_3 \cdot C_6H_8O_7 \cdot H_2O$. Computed %: N 7.45.

The hydrochloride of the β-diethylaminoethyl ester of β-(5-aminonaphthyl-1)-propionic acid. 1 g of the hydrochloride of the β-diethylaminoethyl ester of β-(5-nitronaphthyl-1)-acrylic acid was dissolved in 100 ml of 96% ethyl alcohol. To the solution, which had a yellow color, there was added 1.5 g of nickel catalyst (Raney) suspended in 20 ml of 96% ethyl alcohol. The reaction mixture was placed in a flask with a volume of 500 ml, connected to the glass apparatus usually used for hydrogenation, and agitated in hydrogen for 1.5 to 2 hours. The theoretical amount of hydrogen, 237 ml, was absorbed, although it was observed that the rapid absorption of the gas (177 ml of hydrogen in the first 12 to 15 minutes) was not at first accompanied by a change in the color of the solution. The remaining 60 ml of hydrogen was absorbed in the course of the following 1.5 hours with gradual decolorization of the solution. At the end of the hydrogenation, a completely colorless solution was obtained, which was filtered to remove the catalyst. The alcohol was then driven off in vacuum, and the residual oily material was rubbed in absolute ether and converted into a yellow-rose powder (0.8 g). This was filtered off from the ether, dried in a vacuum desiccator, and

recrystallized several times from absolute ethyl alcohol. The hydrochloride of the β-diethylamino ester of β-(5-aminonaphthyl)-propionic acid was in the form of lustrous pale rose crystals with m.p. 159.5 to 160.0°, very soluble in water and ethyl alcohol, almost insoluble in ether.

3.346 mg substance: 0.246 ml N_2 (21°, 728.6 mm).
4.850 mg substance: 0.336 ml N_2 (21.5°, 745 mm).
Found %: N 8.18, 7.88.
$C_{19}H_{27}O_2N_2Cl$. Computed %: N 7.98.

SUMMARY

1. A new method has been given for the separation of 5-nitro- and 8-nitronaphthyl aldehydes.

2. β-(5-nitronaphthyl-1)-acrylic acid has been obtained, along with its simplest derivatives, several alkamino esters, and dialkylaminoalkyl amides.

3. Several alkamino esters and dialkylaminoalkylamides of β-(5-aminonaphthyl-1)-acrylic acid have been obtained.

4. The β-(x-nitronaphthyl-1)-acrylic acid obtained previously has been shown to be β-(5-nitronaphthyl-1)-acrylic acid.

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A STUDY OF SULFONATION

XIII. THE HYDROLYSIS OF SULFONIC ACIDS

A. A. Spryskov and N. A. Ovsyankina

Ivanov Chemico-Technological Institute and Ivanov State Medical Institute

The decomposition of sulfonic acids into hydrocarbons and sulfuric acid under the action of water and mineral acids had already been noted in 1870 [1]. In 1901, Crafts [1], studying the hydrolysis of xylene sulfonic acids in the presence of hydrochloric and sulfuric acid, found that the presence of mineral acids very considerably hastened the hydrolysis of sulfonic acids. He also noted that the sulfonic acids themselves had a catalytic effect upon the velocity of the reaction. Crafts expressed the supposition that only undissociated molecules of the sulfonic acid underwent hydrolysis. He did not consider the mineral acids as catalysts in the usual sense of this word but supposed that they were agents depressing the dissociation of the sulfonic acids. Later Crafts [3] gave an empirical formula for the velocity constant of hydrolysis of sulfonic acids. This, however, was not found to be applicable.

It is known that sulfonic acids do not hydrolyze at ordinary temperatures. Decomposition begins only upon heating to a definite temperature which depends on the nature of the sulfonic acid. Thus, N.N.Vorozhtsov and V.M.Krasova [4] found that "a concentration of 38% sulfuric acid is the highest boiling acid by which naphthalene β-sulfonic acid is not appreciably hydrolyzed in 5 hours". As 38% sulfuric acid boils at about 113°, it follows that the decomposition of the β-sulfonic acid can be observed only above this temperature. According to the findings of V.N.Ipatiev and A.Petrov, benzene sulfonic acid is hydrolyzed at 170°, benzene disulfonic acid at 330° [5]. m-Xylene sulfonic acid is hydrolyzed at 122°, p- and o-xylene sulfonic acids at 175° [6]. According to the experiments of N.M.Kizhner [7], the hydrolysis temperature of the o-xylene sulfonic acid is 150°. However, Vesely and Stojanova found that the temperature of decomposition of benzene sulfonic acid was 227°, while the temperature for m- and o-xylene sulfonic acids was 137 and 175°, respectively, etc. As the velocity of hydrolytic cleavage depends not only on the temperature but on the proper type of decomposition at the definite temperature, the hydrolysis takes place in such a way that the determination is carried out under different conditions. The conditions of hydrolysis to which reference is made are: temperature, concentrations of sulfonic acid, nature and concentration of mineral acid, and duration of the reaction. All of these influence the results, i.e., they influence the amount of sulfonic acid hydrolyzed.

Friedel and Crafts [5] expressed the opinion that the ease with which hydrolysis takes place depends directly on the ease of formation of the given sulfonic acid. Vesely and Stojanova [8], on the basis of the results of their

determinations, confirm this opinion. For example, the sulfonic acids of nitrobenzene, o-nitrobromobenzene, and other compounds difficult to sulfonate, do not undergo hydrolysis at all. We must, however, note that these experiments were carried out in the presence of phosphoric acid, whose influence on hydrolysis is not the same as that of sulfuric acid. Thus, V.A.Lenkhold [9], who hydrolyzed the sulfonic acid of nitro-m-xylene in sulfuric acid, did not succeed in hydrolyzing it in hydrochloric and phosphoric acids.

V.V.Kozlov [10] showed recently that the α-sulfonic acid of anthraquinone was hydrolyzed (without the presence of mercury) at 180 to 190°; the β-isomer and the disulfonic acid required higher temperature.

There are no published experimental data with regard to the recently [11] expressed hypothesis that the velocity of desulfonation was independent of the concentration of sulfonic acid and of the nature of the inorganic anion.

In the present work, the course of the hydrolysis of α-naphthalene sulfonic acid was studied in the presence of different amounts of water and different amounts of aqueous solutions of sulfuric acid. The desulfonation of sulfosalicylic acid, chlorobenzene sulfonic acid, and β-naphthalene sulfonic acid was also studied. A number of experiments was planned for the purpose of determining the temperature of hydrolysis of the various sulfonic acids.

Hydrolysis of α-Naphthalene Sulfonic Acid in the Absence of Mineral Acids

The anhydrous α-sulfonic acid of naphthalene (or its dihydrate) was mixed with water and heated at a temperature of 100° for 4 hours. The results of the experiments are listed in Table 1: they show the relationship between velocity of hydrolysis and the ratio of sulfonic acid and water. In dilute solutions hydrolysis takes place very slowly. At higher concentrations of the sulfonic acid, the reaction velocity increases, but only up to a certain limit, at which the maximum velocity is observed. This is at the approximate ratio of 0.6 mole water to 1 mole of sulfonic acid. If less water is taken for hydrolysis, the velocity begins to decrease steadily. Thus, the optimal ratio for hydrolysis under the conditions of temperature and length of reaction described is 1 mole sulfonic acid to 0.6 mole of water.

TABLE 1

Hydrolysis of the α-sulfonic acid of naphthalene at a temperature of 100° in 4 hours

Expt. No.	Amounts used		α-acid hydrolyzed (in % of amount used)
	α-acid, g	moles water per mole acid	
19	0.3889	0.28	4.7
23	0.4021	0.39	7.2
20	0.3906	0.48	7.6
24	0.4778	0.58	8.5
21	0.4050	0.70	7.4
25	0.3957	0.85	6.0
22	0.4469	1.00	5.0
15	0.4402	2.00	1.8
17	0.4564	3.00	1.0
18	0.3667	5.02	0.3
81	0.3911	9.0	0.15

Hydrolysis of α-Naphthalene Sulfonic Acid in the Presence of Sulfuric Acid

The experiments were carried out by heating the α-sulfonic acid with 78, 60, and 47.5% sulfuric acid, also at a temperature of 100° for 4 hours. Different amounts of the α-acid (from 0.25 to 0.85 g) were added to the sulfuric acid, so that 1 mole of the α-acid was accompanied by from $^1/_4$ mole to 8 moles of water, contained in the sulfuric acid. In the 78% sulfuric acid, no cleavage of the sulfonic acid group was noted, as under these conditions naphthalene is sulfonated with greater velocity than the α-acid is hydrolyzed.

The results of the hydrolysis experiments, given in Table 2, show that in

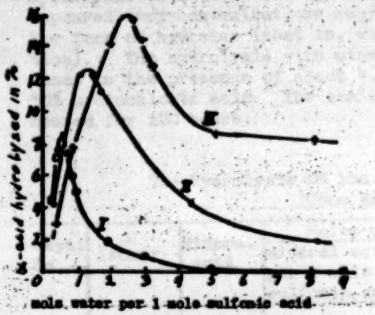

Fig. 1. Results of hydrolysis.

I - with water; II - with 47.5% sulfuric acid; III - with 60% sulfuric acid.

TABLE 2

Hydrolysis of α-sulfonic acid of naphthalene in the presence of sulfuric acid at a temperature of 100° in 4 hours.

Expt. No.	Amounts used: water per 1 mole of α-acid	Amounts used: sulfuric acid per 1 mole of α-acid	Concentration of sulfuric acid used (%)	α-acid hydrolyzed (in % of that used
51	0.39	0.076	60	3.0
49	0.91	0.223	60	7.8
50	2.03	0.530	60	14.2
78	2.71	0.716	60	15.7
52	2.93	0.786	60	14.5
54	3.23	0.889	60	12.9
57	5.15	1.423	60	8.7
89	8.16	2.048	60	8.3
84	0.24	0.041	47.5	4.4
44	0.58	0.089	47.5	7.6
48	1.08	0.176	47.5	12.3
46	1.44	0.239	47.5	12.3
45	1.76	0.292	47.5	11.3
47	4.41	0.749	47.5	4.4
90	8.20	1.366	47.5	2.0

the presence of sulfuric acid also, the velocity of the reaction reaches a maximum at a definite ratio of sulfonic acid and hydrolyzing agent. For different concentrations of sulfuric acid, the maximum velocity is different, and it does not coincide with the maximum velocity of hydrolysis found with water only. In Fig. 1, the results of the experiments carried out are shown graphically in the form of three curves. The first curve gives the results of hydrolysis with water alone, the second with 47.5% sulfuric acid, and the third with 60% sulfuric acid. With the 47.5% acid, the maximum velocity of hydrolysis is reached at the point were 1 mole of the sulfonic acid is in the presence of 1.25 moles of water, contained in the sulfuric acid. With the 60% acid, the maximum is reached with 2.5 moles of water contained in the hydrolyzing agent, per 1 mole of α-acid. The curves show that the maximum velocity of hydrolysis is displaced to the right, i.e., in the direction of increased concentration of the hydrolyzing agent, as the latter's concentration increases, and at the same time these curves show that the absolute value of the velocity of hydrolysis at the maximum point rises considerably with an increase in the concentration of the sulfuric acid.

Thus, in carrying out the hydrolysis of the sulfonic acid, we must not only use a solution of the mineral acid at the highest possible concentration, but we must choose the right amount of it with respect to the sulfonic acid, corresponding to the optimal conditions for the velocity of hydrolysis. At the same time, however, we must take account of the fact that water is used up in the reaction and sulfuric acid formed during the reaction, thus increasing the concentration of mineral acid in the hydrolyzing agent. Thus, in the experiments with 60% sulfuric acid, the concentration of the latter after heating increased by different amounts, but not beyond 66.3% (in Experiment 49).

Determination of the Hydrolysis Temperature of Sulfonic Acids

As has been noted above, it is believed that for every sulfonic acid there is a definite temperature at which it acquires the ability to split off a sulfonic acid group by hydrolysis. We attempted to determine this hydrolysis temperature

for a number of sulfonic acids. For this purpose, we added, in the case of hydrolysis with water alone, 1 mole of water per 1 mole of sulfonic acid; this appeared very convenient, as many of the sulfonic acids are easily obtained in the form of hydrates (that is, with a single molecule of water of crystallization). The hydrolysis with mineral acid was carried out in the majority of cases in the presence of about 4.5 moles of water per 1 mole of sulfonic acid in 30% hydrochloric acid. The sealed tubes containing the reaction mixtures were heated for 100 hours.

TABLE 3

The Hydrolysis of the α- and β-Sulfonic Acids of Naphthalene Upon Heating for 100 Hours.

Expt. No.	Isomer	Mineral acid	Moles used: Mineral acid per 1 mole sulfonic acid	Moles used: Water per 1 mole of sulfonic acid	Concentration mineral acid, %	Temperature	Sulfonic acid hydrolyzed (in % of that used)
82	α-Acid	HCl	0.291	2.22	20.9	65°	0.2
31	α-Acid	H_2SO_4	0.293	1.44	52.5	72	3.2
27	α-Acid	–	0	1.00	0	78	0.2
28	α-Acid	H_2SO_4	0.313	1.47	53.7	78	16.2
153	α-Acid	HCl	1.027	4.88	29.9	113	85.3
9	β-Acid	–	0	1.00	0	117	0
85	β-Acid	HCl	1.026	4.90	29.8	113	1.7

In Table 3 are listed the results of the experiments with α- and β-naphthalene sulfonic acids. Without mineral acid, in the presence of 1 mole of water, the β-sulfonic acid was not at all hydrolyzed at 117°. The hydrolysis of the β-acid in the presence of hydrochloric acid became noticeable at 113°. The hydrolysis of the α-acid under the same conditions took place 50 times as rapidly (Expts. 153 and 85). In the presence of water alone, there was practically no hydrolysis at 78°, that is, during this experiment (27) about 0.002% of the α-acid used in the reaction was hydrolyzed per hour. In the presence of mineral acid, hydrolysis took place above 70° with perceptible velocity (Expts. 31 and 28), and only at a temperature of about 65° was there again practically no reaction in the presence of the mineral acid, so that here only 0.002% of the sulfonic acid used in the reaction was hydrolyzed per hour.

Table 4 gives the results of the hydrolysis experiments with p-sulfosalicylic acid; these results show that after heating for 100 hours in the presence of 1 mole of water, hydrolysis became noticeable only at a temperature of 100°.

In the presence of 30% hydrochloric acid, hydrolysis could be noted at 63° and 70°, but to a very inconsiderable degree, and only at 86° did the reaction take place to a significantly more rapid degree. These experiments show a very great difference both in the velocity of hydrolysis and in the temperature at which hydrolysis begins, when it is carried out with water alone and with hydrochloric acid. Fig. 2 shows two curves, picturing the results of hydrolysis of sulfosalicylic acid with water (Curve II) and with hydrochloric acid (Curve I).

Finally, a number of hydrolysis experiments were carried out with p-chloro benzene sulfonic acid. The results of these experiments, listed in Table 5, show that only at a temperature of 100° is there an appreciable difference between the results of hydrolysis carried out in the presence of water alone and in the presence of hydrochloric acid. At 113, 125, and 140°, the velocity of hydrolysis is very close to the same for both cases. Thus, if the presence of

TABLE 4

The Hydrolysis of p-Sulfosalicylic Acid Upon Heating for 100 Hours

Expt. No.	Moles of water per 1 mole of sulfonic acid	Concentration of HCl, (in %)	Temperature	Sulfonic acid hydrolyzed (% of that used)
94	1.05	0	63°	0
107	1.04	0	70	0
141	1.05	0	86	0
130	1.05	0	101	2.8
91	1.04	0	112	17.6
95	4.63	30.4	63	0.3
108	4.65	30.4	70	0.5
142	4.63	30.4	86	26.9
131	4.64	30.4	101	72.0
92	4.67	30.4	112	88.7

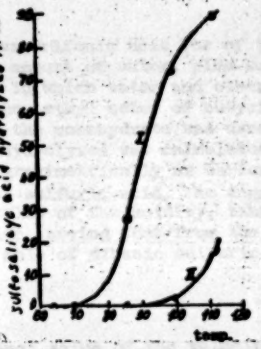

Fig. 2. Results of the hydrolysis of sulfosalicylic acid:

I - with hydrochloric acid; II - with water.

mineral acid shows a considerable influence on the velocity of hydrolysis of α- and β-sulfonic acids of naphthalene, of sulfosalicylic acid, and of other sulfonic acids, in the case of the hydrolysis of chlorobenzosulfonic acid this influence is hardly noticeable. The hydrolysis of chlorobenzene sulfonic acid with water, with 30% hydrochloric acid, and with 60% sulfuric acid, takes place in almost the same way.

TABLE 5

Hydrolysis of p-Chlorobenzene Sulfonic Acid

Expt. No.	Moles of water used per 1 mole of sulfonic acid	Concentration of HCl, %	Temperature	Duration of heating, hours	Sulfonic acid hydrolyzed (in % of that used)
138	1.13	0	101°	100	0
139	4.33	29.4	101	100	0.59
143	1.13	0	113	25	0.74
144	4.48	29.6	113	25	0.54
147	1.13	0	125	25	0.88
148	4.47	29.6	125	25	0.85
171	1.13	0	140	25	1.01
172	4.35	29.4	140	25	1.26
174[1]	4.54	59.5	140	25	1.40

Everything that has been said indicates that the hydrolysis temperature of the sulfonic acid, i.e., the lowest temperature at which the given sulfonic acid shows the ability to hydrolyze, is not a sharply expressed constant, like, for example, the melting or boiling point of a compound. The hydrolysis temperature of any sulfonic acid can be defined only by the arbitrary value of the velocity of hydrolysis during various definite conditions (of amount, concentration, and nature of the mineral acid).

[1] Test 174 performed in the presence of sulfuric acid.

EXPERIMENTAL

A sample of from 0.25 to 0.85 g of the anhydrous sulfonic acid (or of its hydrate) was heated in a sealed tube with a definite amount of water, plus sulfuric or hydrochloric acid in Eikman's apparatus [12] in which water and other liquids were kept boiling (chloroform, alcohol, xylene, ethyl ester of butyric acid, etc.). During the hydrolysis with water alone the monohydrate was used in the majority of cases. The amount of sulfonic acid hydrolyzed was calculated from the amount of sulfuric acid formed, determined gravimetrically as barium sulfate. In experiments conducted in the presence of sulfuric acid, the degree of hydrolysis was determined volumetrically by the value of the acidity, that is by titration with a 0.1 N solution of sodium hydroxide (seeing that from the hydrolysis of 1 mole of a monobasic sulfonic acid 1 mole of dibasic sulfuric acid is formed).

SUMMARY

1. In the hydrolysis of sulfonic acids, a maximal value of the velocity of the reaction is observed in the presence of definite amounts of hydrolyzing agents (water or mineral acids containing water).

2. The position of the maximum reaction velocity depends on the concentration of the mineral acid used for hydrolysis.

3. The degree of hydrolysis of the α- and β-sulfonic acids of naphthalene of sulfosalicylic acid, and of chlorobenzene sulfonic acid has been determined under various conditions.

4. It has been noted that the presence of mineral acid does not always increase the velocity of hydrolysis. Thus, the hydrolysis of chlorobenzene sulfonic acid with water, with 30% hydrochloric acid, and with 60% sulfuric acid takes place at almost the same speed.

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THE CHARACTERISTICS OF α,β-UNSATURATED KETONES. VI

V. L. Esafov

Organic Chemistry Laboratory of the Ural State University. Sverdlov.

I

An investigation of the introduction of bromine and iodoxy groups into α,β-unsaturated ketones* [1] and into diene hydrocarbons with a conjugated system of double bonds [2] has shown the great variety of properties of the various members of both groups of compounds, beginning with their specific behavior as compounds with conjugated systems, and ending with the practically autonomous reaction of the)C=C(and C=O bonds, that is, in the latter case they react like diolefins hardly distinguishable from compounds with isolated double bonds. The accumulated data makes it possible to generalize the various previously observed rules concerning the influence of the structure of the skeleton on the tendency of the given compounds to react, into a general theory on the relationship of the chemical properties to the degree of conjugation of the multiple bonds. It is pertinent to note that the degree of conjugation of multiple bonds has shown itself to be a sufficiently powerful factor to be reflected even in the course of reactions which are not specific for the conjugated system composed of the)C=C(and C=O bonds, as in the introduction of iodoxy and bromine groups, which are typical reactions for the ethylene bond, and in the Grignard reaction, which is characteristic of carbonyl compounds.

It appears necessary to find confirmation for the regularities revealed from our study of typical reactions for compounds with conjugated)C=C(and C=O bonds, and therefore we have chosen for the α,β-unsaturated carbonyl compounds the very characteristic reaction of hydrolytic cleavage, which takes place both in acid and in alkaline medium.

II

Taking into consideration the fact that the formation of α,β-unsaturated aldehydes and ketones takes place through the intermediate stage of the β-hydroxycarbonyl compounds, i.e., that aldol-formation precedes crotonic system formation, we must accept the fact that the socalled "crotonic condensation" is not a characteristic type of condensation process, and by the term "crotonic system formation"** we must understand the process of dehydration of the various β-hydroxycarbonyl compounds.

On the basis of the interrelationship between the process of aldol-formation and crotonic system formation it has been proposed [3] that the reverse process of hydrolytic cleavage of the α,β-unsaturated carbonyl compounds be considered as taking place by means of the intermediate stage of β-hydroxy carbonyl compounds and be assumed to consist entirely of two reactions – the hydration

*For ketones and the Grignard reaction.

**Paying a tribute to tradition.

of the α,β-unsaturated oxo compound, with its conversion into a β-hydroxyoxo compound (I), and the hydrolytic cleavage of the β-hydroxyoxo compound (II), according to the scheme:

$$RCH{=}CHCOR + H_2O \rightleftharpoons RCH(OH)CH_2COR \qquad (I)$$

$$RCH(OH)CH_2COR \xrightleftharpoons{+H_2O} RCHO + CH_3COR + H_2O \qquad (II)$$

The extent of the hydrolytic cleavage of the α,β-unsaturated oxo compound thus depends only on the velocities of the indicated reactions (I and II). In view of the difficulty of investigating reaction (I), we shall thoroughly review the data which have a bearing on reaction (II). The latter may be compared with the thermal cleavage of β-hydroxycarbonyl compounds, which takes place with the formation either of an α,β-unsaturated oxo-compound (A) or of the original compounds (B).

$$RCH(OH)CH_2COR_1 \begin{cases} \xrightarrow{A} RCH{=}CHCOR_1 + H_2O \\ \xrightarrow{B} RCHO + CH_3COR_1 \end{cases}$$

The latter direction (B) of thermal cleavage of the β-hydroxycarbonyl compound in a sense corresponds to their hydrolytic cleavage, and differs by virtue of the fact that during heating there takes place a dissociation of the bonds between the α- and β-carbon atoms, while during hydrolytic cleavage the breaking of this bond takes place under the action of the elements of water in the presence of H^+ or OH^- ions which catalyze the process.

Although the mechanisms of the thermal and hydrolytic cleavage of β-hydroxycarbonyl compounds show differences, all the same they have in common the fundamental fact that dissociation takes place between the α- and β-carbon atoms of the molecule. In this connection, we must decide whether a lesser thermal stability of the β-hydroxycarbonyl compounds is at the same time accompanied by an easier hydrolytic cleavage, or whether, on the other hand, this parallelism may not exist. Unfortunately, the chemical literature is lacking in accurate comparative data [4] with regard to thermal stability, even, for example, for the aldol aliphatic series, but on the basis of the data given, the groups can be arranged in the order of decreasing stability:

$$>C(OH)\underset{H}{\overset{H}{C}}CHO \;\rangle\; >C(OH)\underset{H}{\overset{R}{C}}CHO \;\rangle\; >C(OH)\underset{R}{\overset{R}{C}}CHO,$$

that is, the α,α-dialkylated aldols are most labile. Analogous results are also observed in the β-hydroxy acid series [5]. Here, too, the α,α-dialkylated β-hydroxy acids are most easily split into their components. As for the β-ketols, [6], judging by analogy, these must repeat the general typical properties of β-hydroxycarbonyl compounds, and consequently, the β-ketols with α,α-dialkylated carbon atoms must be most easily cleaved, while the β-ketols with completely hydrogenated α-carbon atoms must be the most difficult to cleave.

β-Ketols of the $>C(OH)\underset{R}{\overset{R}{C}}COR$ type do not fall into the scheme of our study, as they cannot be formed from α,β-unsaturated ketones by hydration, nor can they, by splitting off the elements of water, be transformed into the latter.

Practically, we may consider the β-ketol types:

$$(1)\ RC(OH)\underset{H}{\overset{R}{C}}COR \qquad (2)\ RC(OH)\underset{H}{\overset{H}{C}}COR \qquad (3)\ RC(OH)\underset{H}{\overset{R}{C}}COR \qquad (4)\ RC(OH)\underset{H}{\overset{H}{C}}COR,$$

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*For example - to methyl oxide and its ketone.

of which the first, judging by analogy, might be expected to be most easily cleaved thermally into its components. However, even if we assume that the β-ketol (1) is more easily cleaved by hydrolysis than, for example, the β-ketol (3), it does not entirely follow that the α,β-unsaturated ketone: $\begin{matrix} R & R \\ & \diagdown \\ R & \diagup \end{matrix}$C=CCOR which corresponds to β-ketol (1) will in the last analysis be more easily cleaved than the ketone $\begin{matrix} R \\ \diagdown \\ \diagup \\ R \end{matrix}$C=CHCOR, which corresponds to β-ketol (3). The fact is that the β-ketols themselves are products of hydration of the α,β-unsaturated ketones, specific for the conjugated system of >C=C< and C=O bonds, and dependent on the degree of this conjugation.

It was shown previously [1] that the degree of conjugation decreases from ketones of the type RCH=CHCOR through the ketones R RC=CHCOR to the trialkyl substituted ketones: $\begin{matrix} R \\ \diagdown \\ \diagup \\ R \end{matrix}$C=CCOR.

The velocity of the hydration of ketones of the latter type to give β-ketols, in view of the weak conjugation of the >C=C< and C=O bonds, must be small in comparison with the velocity of the hydrolytic cleavage of the β-ketols, and in the long run this also determines the extent of their hydrolytic cleavage, which must be lowest in ketones of the type under consideration.

On the other hand, with ketones of the type RCH=CHCOR, which show a higher degree of conjugation of the >C=C< and C=O bonds, the hydration must take place more easily, and therefore the amount of cleavage per unit of time will be greater with such ketones than with ketones with less conjugation of the >C=C< and C=O bonds.

III

Turning to the experimental work intended to confirm the above hypotheses on the relation of the hydrolytic cleavage of α,β-unsaturated ketones to the degree of the conjugation between the >C=C< and C=O bonds in their molecules, we faced rather complicated problems in investigating the complicated equilibria which exist during hydrolysis, and include, in addition to the original α,β-unsaturated ketone, the β-ketol, and the cleavage products, i.e., aldehydes and ketone, or a mixture of ketones, or in the simplest case, ketone alone.*

Having taken this circumstance into account, as well as the fact that in carrying out the hydrolysis in acid medium we should be forced to deal with a still more complicated mixture of components participating in the equilibrium**, the study of the hydrolysis of α,β-unsaturated ketones was carried out in alkaline medium. But even in working with moderately alkaline media, we observed that hydrolysis of the ketones RCH=CHCOR was considerably complicated by increasing side reactions.

Having no better course to choose, we utilized for comparison of the extent of hydrolytic cleavage of α,β-unsaturated ketones only such of the ketones as, either because of their own structure or because of the saturated methylketones they formed by hydrolysis, could be estimated by the iodoform reaction, carried out in the manner described by Messinger [7].

These investigations were the first attempts to show experimentally the relation between the degree of conjugation of the >C=C< and C=O bonds in the molecules of the unsaturated ketones and their tendency to undergo hydrolytic cleavage.

*For example, in the case of mesityl oxide and ketones like it.

**As the result of the formation of new condensation products.

It appears to us that the experimental data confirm the hypotheses expressed above. However, we believe that we shall have to include in our investigation a considerably greater number of representatives of the α,β-unsaturated ketones, and in addition, that we shall have to subject to investigation a number of the allied questions which arise during the consideration of the results of the present investigation.

EXPERIMENTAL

The first series of experiments on the investigation of the degree of hydrolytic cleavage of α,β-unsaturated ketones was carried out* with samples of freshly distilled ketones, mostly weighing between 0.14 and 0.24 g. These were placed in ampoules. Then 10 ml of water or 10 ml of aqueous 1.0 N or 0.1 N solutions of NaOH were added and the ampoules sealed and heated for 2 hours on the boiling water bath. After cooling, the contents of the ampoules were filtered through a moist filter. 2 ml of the filtrate was diluted with water to 100 ml, and 10 ml samples of the latter taken for the purpose of carrying out the iodoform reaction. The determination was carried out according to Messinger's directions.

We must note that with this method, the amount of undissolved α,β-unsaturated ketones remained uninvestigated, and that therefore the calculations of experimental data based on the amount of sample used in the experiment, have a conditional character.

For all the ketones which are cleaved by hydrolysis with the formation of saturated methyl ketones, including the case where α,β-unsaturated ketone is itself a methylketone and can therefore be estimated directly by means of the iodoform reaction, as well as the case where it is not a methylketone, the experimental data refer to the using up of $6I_2$ per molecule of the original α,β-unsaturated ketone.

For the ketones which are cleaved to give aldehyde and methylketone, the experimental data refer to the using up of $4I_2$ per molecule of the original α,β-unsaturated ketone, of which $3I_2$ correspond to the molecule of methylketone and I_2 to the molecule of aldehyde, the latter being oxidized, according to our assumptions, to the corresponding acid:

$$I_2 + 2NaOH \longrightarrow NaI + NaOI + H_2O$$

$$RCHO + NaOI \longrightarrow RCOOH + NaI$$

The data of Table 1 show that butylideneacetone and oenanthylideneacetone, because of their low solubility in water, undergo very little hydrolytic cleavage as judged by the iodoform reaction, but show a great tendency to hydrolysis in alkaline media. It is also worth noting that the hydrolysis of butylideneacetone takes place more nearly completely in 0.1 N than in 1.0 N NaOH solution. In the latter case, a considerable amount of tar is formed in the ampoules.

With a number of ketones of the mesityl oxide type, an increase in the molecular weight is accompanied by a decrease of the solubility in water, and along with this, the amount of their hydrolytic cleavage is also lowered. Ketones of this type are better hydrolyzed in the presence of more concentrated solutions of alkali.

*With the help of student E. V. Gorbunova.

TABLE 1

Investigation of the Hydrolytic Cleavage of α,β-Unsaturated Ketones *

Expt. No.	Name and weight of ketone grams	No. of ml of 0.1N $Na_2S_2O_3$ used per 25 ml of iodine solution in blank test	No. of ml of 0.1 N $Na_2S_2O_3$ solution used in actual experiment	Amount of unsaturated ketone undergoing hydrolytic cleavage, (% of theory)
	Butylideneacetone			
1	0.1436	27.37	27.30	3.41
2	0.1688	27.37	26.60	31.95
3	0.1792	27.37	26.22	44.96
	Oenanthylideneacetone .			
1	0.2232	22.70	22.63	3.01
2	0.1744	22.70	22.33	20.43
	Mesityl oxide ..			
1	0.1698	22.70	21.00	40.87
2	0.1842	22.70	19.03	81.46
	3-Methylhepten-3-one 5			
1	0.1170	22.70	22.40	13.39
2	0.2178	22.70	21.16	37.15
	4-Methylnonene-4-one-6 .			
1	0.1576	22.70	22.50	8.15
2	0.1768	22.70	22.24	13.30
	3,4-Dimethylhexene-3-one-5			
1	0.2110 ,.....	21.64	21.38	6.47
2	0.1684	21.64	21.35	9.04

As representatives of the third group of unsaturated ketones, 3,4-dimethylhexene-3-one-5 was chosen. This showed a lesser tendency to hydrolysis than did the ketones of the previous groups.

In view of the fact that in the first series of experiments no study was made of the absolute quantity of α,β-unsaturated ketone going into solution, a second series of experiments** was carried out, chiefly with the ketones*** of lower molecular weight, and with such weights of sample as to permit the ketone

* Hydrolysis carried out in the following media: In experiments numbered 1, 10 ml of water; numbered 2, 10 ml of 1.0 N NaOH; numbered 3, 10 ml of 0.1 N NaOH.

** With the aid of student laboratory assistant, V. V. Molchanova.

*** The experiments were carried out with freshly distilled ketones.

TABLE 2

A Study of the Hydrolytic Cleavage of α,β-Unsaturated Ketones Using Small Samples*

No. of experiment	Name and weight of ketone (g)	No. of ml of 0.1 N $Na_2S_2O_3$ sol. used to titrate 25 ml iodine sol. in blank test	No. of ml of 0.1 N $Na_2S_2O_3$ solution used in actual experiment				Amount of α,β unsaturated ketone hydrolytically cleaved (in % of theory)			
			Duration of Experiment							
			15 sec.	1 min.	5 min.	15 min.	15 sec.	1 min.	5 min.	15 min.
	Butylideneacetone									
1	0.0361	23.28	22.33	21.60	21.60	21.59	36.88	61.33	61.33	61.33
2	0.0287	23.28	–	–	–	21.50	–	–	–	86.91
3	0.0309	23.28	–	–	–	21.66	–	–	–	73.50
	Oenanthylideneacetone									
1	0.0526	23.00	22.21	21.49	21.29	21.19	28.94	55.33	62.65	66.32
2	0.0326	23.00	–	–	–	21.63	–	–	–	81.03
3	0.0352	23.00	–	–	–	21.69	–	–	–	71.71
	Mesityl oxide									
1	0.0311	23.28	22.65	22.23	21.72	21.58	16.56	26.81	41.0	44.68
2	0.0245	23.28	–	–	–	22.02	–	–	–	75.43
3	0.0298	23.28	–	–	–	19.97	–	–	–	90.78
	3-Methylhepten-3-one-5									
1	0.0423	23.28	22.93	22.73	22.06	21.54	8.69	13.66	30.31	43.23
2	0.0276	23.28	–	–	–	21.70	–	–	–	60.16
3	0.0357	23.28	–	–	–	20.15	–	–	–	92.16
	3,4-Dimethylhexene-3-one-5									
1	0.0440	23.28	22.87	22.31	21.91	21.69	9.78	23.17	32.72	37.98
2	0.0328	23.28	–	–	–	22.11	–	–	–	37.49
3	0.0352	23.28	–	–	–	21.72	–	–	–	46.58

to dissolve entirely, at the end of the experiment, in 100 ml of water. At the same time, as far as possible, attention was paid to the relative concentrations of solutions of α,β-unsaturated ketones.

The samples of ketones in sealed ampoules were heated for 2 hours on the boiling water bath with 10 ml of water or 10 ml of 0.01 N or 0.1 N NaOH solution. After cooling, the ampoules were opened, and their contents poured into a calibrated flask, into which water was poured in such a way as carefully to wash out the ampoule, the solutions being made up to 100 ml. In order to carry out the iodoform reaction, 10 ml samples of the solutions thus obtained were used. The determination was carried out according to Messinger's directions. For aqueous solutions of α,β-unsaturated ketones measurements were made after contact with the alkaline solution of iodine for 15 seconds, 1 minute, 5 minutes, and 15 minutes. In view of the incomplete solubility of the sample of oenanthylideneacetone in 95 ml of water, there was carefully added to the solution, without mixing the layers, 5 ml of chemically pure methanol, and the oily drops

* Hydrolysis was carried out in the following media: In experiments numbered 1, 10 ml of water; numbered 2, 10 ml of 0.01 N NaOH; numbered 3, 10 ml of 0.1 N NaOH.

floating on the surface of the aqueous solution were dissolved in it. The solutions were then shaken energetically to give a very fine emulsion, with which the measurements were carried out.

The experimental data of Table 2 show that butylideneacetone and oenanthylideneacetone are determined by Messigner's method after even one minute of contact with the alkaline iodine solution; for butylideneacetone, further standing does not change the results. It is not yet possible to say whether this result is related to the secondary reactions in which the fatty acid aldehyde formed by hydrolysis takes part, or to still other reactions.

Of the three groups of ketones represented, butylideneacetone and oenanthylideneacetone showed a much greater sensitivity to the action of hydrolyzing agents, their hydrolysis taking place more completely in the presence of 0.01 N NaOH solution, and in this case the extent of their hydrolytic cleavage was higher than for the ketones of the other groups. In fact, it is even higher than the tabulated data indicate, as upon preliminary heating with 0.01 N NaOH solution the aldehyde set free by hydrolysis can take part in various reactions such as dismutation, condensation, and tar-formation, and therefore, when the iodoform reaction is later carried out, the iodine used up reacted almost entirely with the acetone, although in the calculations it was assumed (cf. above) that one fourth of the total iodine used up reacted with the aldehyde.

In the presence of 0.1 N NaOH solution, the hydrolytic cleavage of the indicated ketones is accompanied by a number of side reactions, including tar formation. In this case, the hydrolysate is in the form of a stable emulsion, including very fine drops of tar. Because of this, the general picture of the hydrolysis is distorted, and considered apart, it is not an index of the given group of ketones (cf. Table 1).

In going over to the data to be considered for ketones of the mesityl oxide type, the first thing that strikes us is the tendency of the α,β-unsaturated ethyl ketone, 3-methylheptene-3-one-5 to give a positive iodoform reaction*. This is related to its hydrolytic cleavage to form methylethyl ketone; during this process, after 15 minutes the results for this ketone and mesityl oxide are considerably equalized. It must be shown by further investigations whether or not these results are generally valid for this type of ketone. A comparison of the results for the given ketones also gives rise to the question of the sequence of the reaction for the formation of iodoform and of hydrolysis. It is clear, further, that the hydrolysis of this type of ketone takes place more completely under more severe conditions, but as with the preceding group of ketones, does not reach 100% because of the reversibility of hydrolysis. Finally, 3,4-dimethylhexene-3-one-5, despite the fact that it belongs to the methyl ketones, is more weakly hydrolyzed than 3-methylheptene-3-one-5. Its preliminary heating with a 0.01 N NaOH solution does not result in any reaction; a small increase in the extent of its hydrolytic cleavage takes place only with a 0.01 N NaOH solution. Thus, this ketone, with regard to the extent of its hydrolysis takes last place.

SUMMARY

1. It has been shown that α,β-unsaturated ketones with normal structure are better hydrolyzed in the presence of 0.01 than of 0.1 N NaOH solution. Ketones of the mesityl oxide type, on the other hand, are more completely hydrolyzed by a 0.1 N solution of NaOH. Upon trialkylvinyl ketones, 0.01 N NaOH solution has no action, the hydrolysis taking place only under the action of a 0.1 N NaOH solution.

2. The indicated characteristics of the behavior of α,β-unsaturated ketones

*With 0.1 N NaOH solution, the ketone does not give iodoform after standing for 15 minutes.

may be utilized for analytic purposes, for the determination of their structural types.

3. It has been shown that α,β-unsaturated ketones of normal structure, as possessors of a high degree of conjugation of the)C=C(and C=O bonds, undergo hydrolytic cleavage under more gentle conditions, and to a greater extent, than ketones of the mesityl oxide type, and that these latter, in their turn, hydrolyze better than representatives of the trialkylated vinyl ketones.

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THE SYNTHESIS OF RACEMIC OXIDES OF N-PROPYL- AND N-ISOPROPYLTETRAHYDROQUINOLINE

Ya. Ya. Dodonov, N. K. Pado, K. K. Petelina and N. M. Petrova

Laboratory of General and Inorganic Chemistry of the N. G. Chernishevsky Saratov State University

After Meisenheimer succeeded in separating into optically active stereoisomers the methylethylaniline oxide [1] he had synthesized, interest grew considerably in the amine oxides of asymmetrical structure, stimulated chiefly by the endeavor to determine the quantitative relationship between the rotation of the representatives of this group of compounds and the size and character of the organic radicals attached to the nitrogen. However, it has been impossible up to the present to determine definite regularities in this case, partially because of the negative results of such experiments in various individual cases, despite the presence in the molecules of various organic radicals [2] attached to the nitrogen.

One of us has previously succeeded in synthesizing and splitting into optically active stereoisomers the oxide of N-methyl tetrahydroquinoline (kairoline) [3], and then that of N-ethyl tetrahydroquinoline [4] as well. It is in place here to note on the one hand the extraordinary ease of the separation of the first of these bases by combining them with two optically active acids – d-K-bromocamphorsulfonic and d-tartaric acids – and on the other hand the fact that the optically active oxides of kairolene were uniquely obtainable in the free state, while in all other cases it was possible to deal only with salts of the oxides or with the bases obtained from these by the action of alkali only in aqueous solutions [2]. The measurements of the rotation, both of the salts of these oxides as well as of the free bases, showed a considerable decrease in the angle of rotation of the plane of polarization in passing from the oxide of kairolene to the oxide of N-ethyltetrahydroquinoline, i.e., upon replacing the methyl radical in the molecule by the ethyl radical.

Thus, if the molecular rotation of the hydrochlorides of kairolene N-oxide equals $\pm$ 88°, then for the same salts of the N-oxide of ethyltetrahydroquinoline, it equaled $\pm$ 65°; the corresponding values for the free bases were $\pm$ 45° for the first and +41 and −40° for the second. This is obviously related directly to the decrease in the degree of asymmetry in the structure of the molecule in the second case.

The realization of the syntheses of the oxides of N-propyl and N-isopropyltetrahydroquinolines described in this communication was conditioned by the attempt further to split them into their optically active stereoisomers, and thus to show the influence of the substitution of the methyl and ethyl radicals by propyl and isopropyl on the change in the degree of asymmetry of the molecule

so far as this might be reflected in the rotation of the compounds obtained.

Of the methods now being used to obtain oxides of the tertiary amines – the use of hydrogen peroxide, of Caro's acid, and of perbenzoic acid, we chose the last, which in this case appeared to be most convenient.

EXPERIMENTAL

Salts of the Racemic Oxide of N-Propyltetrahydroquinoline

The picrate. A benzene solution of 6 g of N-propyltetrahydroquinoline which we had synthesized and freed of impurities [5] with a boiling point of 129-130° (4 to 5 mm) was mixed during cooling with ice water with 200 ml of a benzene solution of perbenzoic acid (obtained by the usual method from benzoyl peroxide [6]) containing 0.58 g of active oxygen (somewhat more than the theoretical quantity). After 10 to 15 minutes, there was added to the reaction mixture a benzene solution which had been saturated in the cold with 7.9 g of picric acid. After the greater part of the benzene had been driven off under reduced pressure until the volume had been reduced to approximately 70 to 80 ml, it was considerably diluted with ether, and there precipitated out of the yellow colored solution a copious finely crystalline precipitate of the picrate of N-propyltetrahydroquinoline oxide, colored yellow. The crystals were filtered off under reduced pressure and washed well, first with a small quantity of a mixture of benzene and ethyl ether, then with ether alone, and then kept in a vacuum desiccator over sulfuric acid, activated charcoal, and caustic alkali until they reached constant weight. Yield 12.9 g (about 90%).

The picrate was practically insoluble in water, soluble in acetone in the cold, and much more soluble upon heating, soluble with difficulty at room temperature in benzene and ethyl ether, very soluble upon heating. After recrystallization from acetone, the picrate melted at 117-118° with subsequent decomposition up to 125°.

0.1433 g substance: 0.2693 g CO_2; 0.0627 g H_2O.
0.1561 g substance: 0.2929 g CO_2; 0.0687 g H_2O.
0.1321 g substance: 15.4 ml N_2 (20°, 758 mm).
Found %: C 51.28, 51.21; H 4.90, 4.92; N 13.55
$C_{12}H_{17}ON \cdot C_6H_3O_7N_3$. Computed %: C 51.43; H 4.79 N 13.33.

The hydrochloride. The picrate (3 g) was dissolved in 5 g of nitrobenzene placed in a dropping funnel, and decomposed by shaking energetically with small portions of concentrated hydrochloric acid. To better separate the aqueous solution obtained from the picric acid in the nitrobenzene [4], ethyl ether was added to the reaction mixture. The aqueous solution of the hydrochloride containing an excess of hydrochloric acid was poured into another dropping funnel, in which it was entirely freed from picric acid by carefully shaking with new portions of ether. The ether extracts were in their turn washed with concentrated hydrochloric acid. The solution of hydrochloride obtained freed from picric acid and nitrobenzene, was concentrated under diminished pressure in a small round-bottomed wide-necked flask until it formed a thick syrup. When the latter was kept for several days in a vacuum desiccator over phosphoric anhydride and caustic potash, it began to crystallize. Crystallization was hastened by the addition to the syrup of traces of anhydrous ethyl alcohol and a small amount of acetone. The colorless crystals of hydrochloride obtained were filtered under diminished pressure and washed with a mixture of acetone and ether, then dried to constant weight in a vacuum desiccator over phosphoric anhydride and caustic potash. Yield 1.2 g (about 74%). The compound melted at 137-138° with decomposition, taking on a reddish-brown color.

0.3411 g substance: 19.50 ml baryta water (0.0764 N).
Found %: HCl 15.93.
$C_{12}H_{17}ON \cdot HCl$. Computed %: HCl 16.01.

The di-π-bromocamphorsulfonate. 0.8 g of the hydrochloride was dissolved in a small amount of water and the solution mixed on the water bath with an aqueous solution of the amount of silver bromocamphorsulfonate calculated for the metathetical reaction, until there was no more formation of silver chloride precipitate. The solution of the bromocamphorsulfonate of the N-propyltetrahydroquinoline oxide obtained was concentrated under diminished pressure in a small round-bottomed flask until it formed a thick syrup, which was then allowed to crystallize in a vacuum dessicator over sulfuric acid.

The substance obtained was recrystallized from a small quantity of ethyl alcohol. Under the microscope it was seen to be a mixture of two crystalline forms – platelets and needles. This bespoke the presence of two stereoisomers, salts of the dextro and laevo bases.

Yield 1.58 g (about 90% of the theoretical). M.p. 138-144° (not sharp) with decomposition and formation of a redish-brown color.

0.1401 g substance: 0.2692 g CO_2; 0.0826 g H_2O.
Found %: C 52.44; H 6.59.
$C_{12}H_{17}ON \cdot C_{10}H_{15}O_4BrS$. Computed %: C 52.59; H 6.42.

The small amount of the substance obtained made it impossible for the time being to carry out the separation of the optically active stereoisomers.

Salts of the Racemic Oxide of N-Isopropyltetrahydroquinoline

The picrate. 6.4 g of the freshly distilled N-isopropyltetrahydroquinoline we had synthesized [7], with b.p. 119° (6 to 7 mm), was treated, as in a previous experiment, in benzene solution with perbenzoic acid (0.6 g of active oxygen), and the oxide obtained was transformed into the picrate (8.4 g of picric acid). After removal of the greater part of the benzene in vacuum and the addition of ethyl ether, a yellow, finely crystalline precipitate of the picrate separated from the solution. This was filtered off under diminished pressure and washed with ether. The picrate weighed 13.8 g (yield about 90%). It was practically insoluble in water, soluble with difficulty in the cold in alcohol, benzene, and acetone, and easily soluble upon heating. After recrystallization from acetone, it melted at 132.5° with decomposition to give a reddish-brown color.

0.1299 g substance: 15.0 ml N_2 (22°, 762 mm).
Found %: N 13.49.
$C_{12}H_{17}ON \cdot C_6H_3O_7N_3$. Computed %: N 13.33.

Hydrochloride. 4 g of the picrate was converted into the hydrochloride by the method described for the hydrochloride of the oxide of N-propyltetrahydroquinoline.

Yield 1.8 g (83% of the theoretical). The hydrochloride, recrystallized from a mixture of alcohol and acetone, melted at 143-144°, with decomposition and the formation of a reddish-brown color.

0.3221 g substance: 18.38 ml baryta water (0.0764 N).
Found %: HCl 15.90.
$C_{12}H_{17}ON \cdot HCl$. Computed %: HCl 16.01.

SUMMARY

The picrates and hydrochlorides of the oxides of N-propyl- and N-isopropyltetrahydroquinoline and the d-π-bromocamphorsulfonate of the oxide of N-propyltetrahydroquinoline have been synthesized and their properties described.

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THE REACTION OF ACID HALIDES OF ACYLATED AMINOACIDS WITH HYDROXY COMPOUNDS

M. M. Botvinik and I. S. Severin

From the Laboratory of Protein Chemistry of Academician N. D. Zelinsky, Moscow State University

The hydroxyaminoacids are widely distributed in proteins [1], and therefore the question of the role of the hydroxyl in protein has a basic significance. The investigations of Reitz, Ferrel, Frankel-Conrat and Olcott [2] on the action of sulfuric acid on hydroxyaminoacidsand proteins has very definitely shown that the number of hydroxyl groups corresponds to the amount of sulfuric acid which adds on. However, the conditions under which the experiments were carried out were so severe that they did not exclude the rupture of labile hydroxyl bonds in the protein. This is also true of the experiments on the methylation of protein with dimethyl sulfate [3]. A number of authors have suggested the possibility of the formation of oxazoline rings [4,5].

The nature of the possible forms of hydroxyl group bonds is of great interest, as this group can play a role in non-peptide bonds [6]. Only in phosphoproteins has a bond been found between phosphoric acid and the hydroxyl groups of serine [7]. In the general literature about hydroxyaminoacids we rarely encounter standard experiments on the suggested forms of compounds between the hydroxy group and aminoacid residues. Bergmann and Mickeley [8] describe the formation of oxazoline rings from O-benzoyl derivatives of serine and indicate the possibility of similar reactions in labile protein molecules. However, the attempt to carry out this reaction with peptides containing a hydroxyaminoacid residue did not succeed. Instead of an oxazoline ring, a diketopiperazine was formed.

In the present work, we investigated the reaction of acid halides of acylated aminoacids with hydroxyacids and hydroxyaminoacids in order to obtain an ester bond and to study the properties of such compounds. As an analog of these compounds we may refer to the glycine ethyl ester of hippurylglycolic acid obtained by Curtius and Thompson [9], $C_6H_5CONHCH_2 - COOCH_2CONHCH_2CO_2C_2H_5$, which was formed by the reaction of hippuric acid on the ethyl ester of diazoacetylaminoacetic acid.

The reaction of acid chlorides on hydroxyacids and hydroxyaminoacids has been studied in considerable detail. As far back as 1905, Sorensen and Andersen [10] worked out the conditions for the benzoylation of hydroxyaminoacids in order to obtain mono-N-benzoylated and di-N,O-benzoylated derivatives. But only the investigations of Bergmann [8], Synge [11], and especially Toennies and Kolb and Toennies and Sakami [12] determined the conditions for obtaining O-acylated derivatives of hydroxyaminoacids with free amine groups.

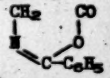
Further, the hydroxy group does not react with all the acylating and alkylating reagents with which the neighboring amino group easily enters into reaction. Thus, the acid chloride of dinitrobenzoic acid reacts neither with the hydroxy group of serine nor with that of lactic acid [13]. Dinitrofluorobenzene is without action on the hydroxy group of serine [14]. $POCl_3$ does not give a phosphoric acid ester with serine.

In this investigation, the experiments were carried out with hippuryl chloride in anhydrous ether, benzene, or xylene. Experiments were carried out with lactic acid ester, with glycolic acid, and with the N-benzoylated derivatives of d,l-serine and d,l-threonine. There was a positive reaction with hydroxy acids. After heating in absolute ether for 10 to 12 hours, hippurylglycolic acid was obtained in 30% yield, m.p. 148-149°, and the ethyl ester of hippuryllactic acid in a yield of 19%, m.p. 105°. Both compounds were relatively unstable. Upon heating with water for 30 minutes, hippurylglycolic acid was 92% hydrolyzed.

On the other hand, the reaction with the N-benzoyl derivatives of serine and of threonine did not take place. N-benzoyl derivatives of the hydroxyaminoacids were heated with hippuryl chloride at three temperatures in absolute ether, benzene, and xylene. In not one of these experiments was the desired compound isolated. In the experiments in ether and benzene media benzoylserine and benzoylthreonine were isolated unchanged. Only traces of hippuric acid were noted, despite the fact that a powerful evolution of HCl was observed during the experiment.

It was necessary to assume that under these conditions, the hippuryl chloride formed an azlactone ring (see equation). In order to decide this, a blank experiment was carried out by heating hippuryl chloride in absolute ether. During this experiment, the same strong evolution of HCl was observed. The heating was continued until the acid chloride was completely used up. The solvent was then removed in vacuum. Upon the addition of aniline to the residue, the anilide of hippuric acid was formed.

$$C_6H_5CONHCH_2COCl \rightarrow$$



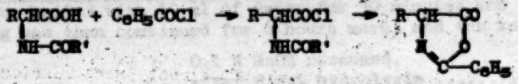
In order to make sure that this reaction held true generally for acid chlorides of acylated amino acids, a similar experiment was carried out with the acid chloride of benzoylalanine. The reaction took place similarly. After it was concluded and the benzene driven off, aniline was added to the residue and the anilide of benzoylalanine obtained.

Thus, azlactone formation took place more easily than the formation of an ester with hydroxyaminoacids. In order to get around this, we carried out an experiment with the acid chloride of N-phenylglycine and N-benzoylthreonine. But in this case, the reaction took place in a different direction, and N-diphenyldiketopiperazine was obtained:

$$2C_6H_5NHCH_2COCl \rightarrow C_6H_5N\begin{matrix}CH_2-CO\\ \diagup\quad\diagdown\\ CO-CH_2\end{matrix}NC_6H_5.$$

The ease of azlactone formation of the acid chlorides of acylated aminoacids gives some basis for the explanation of the formation of azlactones during the benzoylation of aminoacids. Carter, Handler, and Melville [15] found that the action of benzoyl chloride upon N-benzoylthreonine in pyridine solution at 0° gave an azlactone. In 1943, Carter, Handler, and Stevens [16] determined the fact that this was a general reaction. Aminoacids with benzoyl chloride in pyridine give azlactones. In addition, Karrer [17] and his coworkers found that azlactones were formed by the action of the acid chloride of azobenzenecarboxylic acid on leucine and valine in aqueous alkaline medium. The extent of azlactone

formation increased with an increase in the duration of the reaction. Our data permit us to assume that in all these cases, the benzoyl chloride reacts with the acylated aminoacid to form the acid chloride of the benzoylated aminoacid, which then closes the ring to form azlactone:



EXPERIMENTAL

The Reaction of the Acid Chloride of Hippuric Acid With the Ethyl Ester of Lactic Acid

Hippuryl chloride was obtained by Fischer's method [18], with the difference that not acetyl chloride, but carbon tetrachloride was used as solvent, the solvent being first dried over calcium chloride and distilled over sodium. All the experiments were carried out with stirring in the apparatus of N.I.Gavrilov [25], thus permitting us to filter with suction, wash, and dry the substance without the access of air.

The ethyl ester of lactic acid was obtained by the method of Filachione and Longel [18]. B.p. 51-53° at 10 ml. This corresponded to the data in the literature.

3 ml of lactic acid ester, the hippuryl chloride obtained from 2.5 g of hippuric acid, and 40 ml of absolute ether were heated in N.I.Gavrilov's apparatus on a water bath for 10 hours. The evolution of hydrogen chloride was an indication that the reaction began only after an hour. At the end of the reaction, the white precipitate (A) which remained on the bottom was filtered with suction and washed with ether. It gave no reaction for halogen, and had acid properties. After recrystallization from water it had m.p. 184°. Under the microscope it was seen to consist of a single type of needle, characteristic for hippuric acid. A mixed test with hippuric acid had the same melting point.

The ethereal filtrate was concentrated in vacuum, and the precipitate which formed filtered off. It did not give a reaction for halogen, was slightly soluble in water, very soluble in benzene, and slightly soluble upon heating in isooctane. After recrystallization from isooctane, 0.3 g of a white crystalline substance was obtained, very much like cotton wool. Yield 19%, m.p. 106°. The melting point was unchanged after a second recrystallization.

Found %: N 4.46, 4.48.
$C_{14}H_{17}O_5N$. Computed %: N 4.56.

II. The Reaction of the Acid Chloride of Hippuric Acid with Glycolic Acid

1.6 g of glycolic acid, the hippuryl chloride obtained from 2 g of hippuric acid, and 25 ml of absolute ether were mixed in N.I.Gavrilov's apparatus and heated on a water bath for 12 hours. Hydrogen chloride began to be evolved after 2 hours. After the evolution of HCl had ended, the precipitate was filtered off and washed with ether. It weighed 1.2 g. The substance had the properties of an acid, did not contain halogen, was insoluble in benzene and chloroform, and dissolved upon gentle heating in alcohol, water, ethyl acetate, and isoamyl and isopropyl alcohols. M.p. 148-149°; after two recrystallizations, the melting point was unchanged.

Found %: N 5.80.
$C_{11}H_{11}O_5N$. Computed %: N 5.90.

Found: N 244 (titration)
$C_{11}H_{11}O_5N$. Computed: N 237.

The hydrolysis of hippurylglycolic acid. 0.035 g of hippurylglycolic acid was boiled with 10 ml of water for 30 minutes and the solution titrated; heating was then continued for 6 hours more, and the solution again titrated.

0.1 N NaOH consumed.
after first hydrolysis .....1.95 ml,
After second hydrolysis .....0.74 ml.

Total 2.70 ml

$C_{11}H_{11}O_5N$. Computed ml 0.1 N NaOH: 2.96 ml

III. The Reaction of Hippuryl Chloride With N-Benzoyl Derivatives of Hydroxyaminoacids

The reaction with benzoylserine in ether. 1.8 g of benzoylserine, the hippuryl chloride obtained from 2 g of hippuric acid, and 27 ml of absolute ether were heated in N.I.Gavrilov's apparatus on the water bath for 20 hours. After the evolution of hydrogen chloride had ceased and the test for halogen by Beilstein's method was negative, the precipitate was filtered with suction, washed with ether, and dried.

0.1037 g substance: Consumed 4.4 ml 0.1 N NaOH (titration).
(O-hippuryl-N-benzoylserine). $C_{19}H_{18}O_6N_2$. Computed: 2.8 ml 0.1 N NaOH
(N-benzoylserine). $C_{10}H_{11}O_4N$. Computed: 4.9 ml 0.1 N NaOH.
Found %: N 6.95, 6.94.
$C_{19}H_{18}O_6N_2$. Computed %: N 7.56.
$C_{10}H_{11}O_4N$. Computed %: N 6.70.

Thus, the reaction gave 1.6 g of benzoylserine and an insignificant amount of hippuric acid.

The reaction of hippuryl chloride with benzoylserine in benzene. In N.I. Gavrilov's apparatus, 0.4 g of benzoylserine, the hippuryl chloride obtained from 0.43 g of hippuric acid, and 20 ml of absolute benzene were mixed. The reaction took 8 hours. The precipitate obtained was filtered with suction and washed with benzene.

0.1095 g substance: Consumed 4.77 ml 0.1 N NaOH.
(O-hippuryl-N-benzoylserine). $C_{19}H_{18}O_6N_2$. Computed: 2.96 ml 0.1 N NaOH.
(N-benzoylserine). $C_{10}H_{11}O_4N$. Computed: 5.60 ml 0.1 N NaOH.
Found %: N 6.96, 6.94.
$C_{19}H_{18}O_6N_2$. Computed %: N 7.56.
$C_{10}H_{11}O_4N$. Computed %: N 6.70.

The reaction gave 0.38 g of benzoylserine. Traces of hippuric acid were observed.

The reaction with benzoylserine in xylene. 0.95 g of benzoylserine, the hippuryl chloride obtained from 1 g of hippuric acid, and 15 ml of xylene freshly distilled over sodium were heated in N.I.Gavrilov's apparatus for 1 hour 30 minutes on a glycerine bath. Very considerable tarring took place. The reaction was stopped and the precipitate filtered off and washed with chloroform. The precipitate was white, and melted at 179°. After recrystallization from water, it had m.p. 182°. A mixed test with hippuric acid gave a melting point of 180°. No benzoylserine was observed, and it was assumed that azlactone formation took place. The xylene was removed from the solution in vacuum, and 1.0 N hydrochloric acid was added to the residue until there was a definite acid reaction by Congo red. The solution was then heated on the water bath to hydrolyze the azlactone

and the benzoylaminoacrylic acid. The formation of pyruvic acid was detected by the qualitative reaction with salicylic anhydride and alkali, by Straube's method [20].

The reaction with benzoylthreonine in ether. 0.5 g of hippuric acid and 15 ml of absolute ether were heated in N.I.Gavrilov's apparatus on the water bath for 24 hours. The precipitate was filtered off with suction and washed with ether. M.p. 152°.*

0.1014 g substance. Consumed: 4.84 ml 0.1 N NaOH.
(O-Hippuryl-N-benzoylthreonine). $C_{20}H_{20}O_6N_2$. Computed: 2.6 ml 0.1 N NaOH.
(N-Benzoylthreonine). $C_{11}H_{13}O_4N$. Computed: 4.54 ml 0.1 N NaOH.
Found %: N 6.68, 6.61.
$C_{20}H_{20}O_6N_2$. Computed %: N 7.30.
$C_{11}H_{13}O_4N$. Computed %: N 6.27.

0.45 g of unreacted N-benzoylthreonine was recovered.

The reaction of N-Benzoylthreonine in benzene. The experiment was carried out the same way as in ether.

0.1046 g substance: Consumed: 4.80 ml 0.1 N NaOH.
$C_{20}H_{20}O_6N_2$. Computed: 2.70 ml 0.1 N NaOH.
$C_{11}H_{13}O_4N$. Computed: 4.70 ml 0.1 N NaOH.

0.5 g of unreacted N-benzoylthreonine was recovered.

The reaction of the acid chloride of N-phenylglycine on N-benzoylthreonine. The acid chloride of N-phenylglycine was obtained in the same way as the acid chloride of hippuric acid. To the reaction there were added 1.6 g of N-phenylglycine. 2.5 g of phosphorus pentachloride, and 30 ml of carbon tetrachloride freshly distilled over sodium. The mixture was stirred at room temperature for 3 hours. The acid chloride of N-phenylglycine which was formed was filtered with suction and washed with ether; then to it there was added 0.9 g of benzoyl threonine and 40 ml of absolutely dry benzene. The mixture was heated on the water bath for 10 hours. An intense evolution of hydrogen chloride was observed, and a precipitate with a grayish-sandy color formed. At the end of the reaction (negative test for halogen by Beilstein's method) the precipitate was filtered with suction and washed with soda. It recrystallized from alcohol in the form of needles. Yield 0.8 g; m.p. 261°.

According to the literature data [21], N-diphenyldiketopiperazine melts at 263°.

Found %: N 10.2.
$C_{16}H_{14}O_2N_2$. Computed %: N 10.5.

When dilute sulfuric acid was added to the solution, 0.70 g of N-benzoylthreonine precipitated.

IV. The Formation of Azlactones from Acid Chlorides of Acylated Aminoacids

The azlactone of hippuric acid (identified as the hippurylanilide). The hippuryl chloride obtained from 2 g of hippuric acid was heated in 30 ml of absolute benzene on the water bath until the evolution of hydrogen chloride had ceased. The reaction took 6 to 10 hours. During the reaction, the solution tarred considerably. The undissolved precipitate was then filtered off with suction and washed with benzene. It was hippuric acid; m.p. 188°.

The benzene solution was concentrated in vacuum, and to the oil which remained, 1.5 ml of aniline was added. The aniline had been dried over fused caustic potash and distilled over zinc dust. The reaction mixture was heated on a water bath. After cooling, a precipitate formed. This was filtered off

*Amount of benzoylthreonine used is not included in the Russian text. C.B.

and washed with benzene. The white substance obtained was the anilide of hippuric acid; m.p. 212°. According to the literature, the m.p. is 212.5° [22].

Found %: N 10.60.
$C_{15}H_{14}O_2N_2$. Computed %: N 11.0.

The azlactone of benzoylalanine (identified as the benzoylalanine anilide). Benzoylalanine was obtained by the method of Sörensen and Andersen. It melted at 168°. The acid chloride was suspended in 40 ml of dry benzene which had been freshly distilled over sodium and heated on the water bath for 10 hours until the halogen was completely used up. During the heating, the precipitate dissolved very rapidly, and the solution was colored a weak yellow; this remained unchanged until the end of the experiment. The total volume was 50 ml. The benzene was driven off from 25 ml in vacuum, and to the greenish-yellow oil remaining there was added 2 ml of aniline which had been dried and freshly distilled over zinc dust. A considerable evolution of heat was at once observed, and the solution turned orange. After a short period of standing, a finely crystalline precipitate formed, and this was filtered with suction and washed with ether. It was the anilide of benzoylalanine; m.p. 169°. The amount obtained was 0.7 g, or 84%. According to the literature, the m.p. is 175° [23] and 165° [24].

Found %: N 10.38.
$C_{16}H_{16}O_2N_2$. Computed %: N 10.44.

SUMMARY

The acid chlorides of acylated aminoacids react with hydroxyacids and their esters to form derivatives attached to the hydroxyl. This reaction does not take place under the conditions investigated with N-benzoyl derivatives of hydroxyaminoacids. Upon heating in benzene, the acid chlorides of hippuric acid and benzoylalanine form azlactones. By the same method, the acid chloride of phenylglycine is converted into N-diphenyldiketopiperazine.

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TERTIARY ACETYLENE ALCOHOLS

II. DI-p-TOLYLACETYLENYLCARBINOL

I. A. Favorskaya and student L. R. Fedorova

Department of the Structure of Organic Compounds
The A. A. Zhdanov Leningrad State University, awarded the Order of Lenin

The condensation of acetylene with aromatic and fatty aromatic ketones has hardly been investigated. Campbell [1] investigated in detail the reaction between sodium acetylide and ketones in liquid ammonia, and found that in the condensation of acetophenone with acetylene the yield of methylphenylacetylenyl carbinol hardly reached 7%. Upon reacting acetophenone with acetylene in the presence of sodium amide, Carothers [2] obtained the acetylenic alcohol, methylphenylacetylenyl carbinol, in a yield of about 2%. A.I.Zakharova [3] obtained diphenylacetylenyl carbinol in a yield of 30% by condensing benzophenone with acetylene under the conditions of the Favorsky reaction. In addition to the carbinol, there was always obtained during the condensation the acetylene γ-glycol, tetraphenylbutinediol, in yields up to 50%. In addition, part of the ketone was always recovered unchanged.

The objective of this investigation was to study the condensation of para-substituted benzophenones with acetylene. As the first ketone, we chose di-p-tolyl ketone. We synthesized this from carbon tetrachloride and toluene in the presence of anhydrous aluminum chloride.

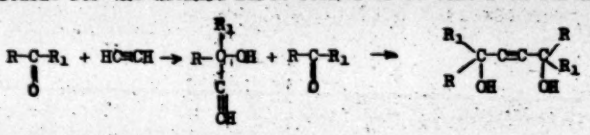
$$2CH_3C_6H_5 + CCl_4 \longrightarrow CH_3C_6H_4CCl_2C_6H_4CH_3 \xrightarrow{H_2O} CH_3C_6H_4\underset{\underset{O}{\|}}{C}C_6H_4CH_3$$

This method gives satisfactory results, and has a great advantage over the old method of synthesis of these ketones from phosgene. The condensation of the di-p-tolyl ketone with acetylene was carried out by the A.E.Favorsky method.

As the chief reaction product we obtained the acetylenic alcohol, di-p-tolylacetylenylcarbinol. The glycol was obtained only as a minor impurity. The absence from the reaction products of glycol and unreacted ketone indicates that the di-p-tolyl ketone reacts energetically with acetylene.

In this respect it resembles the simplest aliphatic ketones. In a detailed investigation of the condensation of acetylene with methylketones of the general formula $CH_3\underset{\underset{O}{\|}}{C}(CH_2)_nCH_3$ under the conditions of the Favorsky reaction, we found, using the three ketones methyl-n-propylketone, methyl-n-butylketone, and methyl-n-nonylketone, that the velocity of condensation decreases with an increase in the molecular weight of the ketone. Along with the increase in molecular weight, the yield of acetylenic alcohol decreases, and the yield of glycol increases.

As an example, we can cite here the condensation of methylnonylketone with acetylene. Condensing the methylnonylketone under the usual conditions, we obtained as the chief reaction product the acetylenic γ-glycol. In addition, a considerable part of the ketone was recovered unchanged. The velocity of the reaction of the ketone with acetylene was so slight that the ketone was always present in excess in the reaction medium, and consequently, all the conditions were suitable for the alcohol first formed to be converted further into the glycol:



We were able to obtain methylnonylacetylenylcarbinol only when we greatly increased the dilution of ketone in the solvent, and decreased the velocity of its addition to the reaction mixture. In comparing the reaction of benzophenone with acetylene with the reaction of the aliphatic methylketones $CH_3-\overset{\overset{O}{\|}}{C}-(CH_2)_n-CH_3$ we see that benzophenone, like the higher methylketones, takes part in condensation slowly, and that as a result there is always present during the reaction a mixture of ketone, carbinol, and glycol. When two methyl groups are introduced into the para position, as in the case of di-p-tolyl ketone, the ability of the ketone to react is increased to such a degree that it reacts with acetylene in the same way as does acetone.

Turning our attention again to the condensation of di-p-tolyl ketone with acetylene, we shall dwell in more detail on the indications of the structure of the di-p-tolylacetylenylcarbinol.

Di-p-tolylacetylenylcarbinol was obtained by us for the first time. The carbinol melts at 86 to 87°. A mixed test with the ketone melted at 56 to 58°. The literature gives the following data with regard to tetratolylbutinediol: G.Arbuzov and T.Temnikova [4] determined its melting point to be 156°. R. Kuhn [5] gives for the glycol a melting point of 78°. In a review by Johnson [6], only Kuhn's results are given. Apparently we must assume that Kuhn had not a pure product but a eutectic mixture of the glycol and the ketone, as his data are based only on an elementary analysis. But as the percentages of carbon and hydrogen for ketone, glycol, and carbinol are very close, it is impossible, on the basis of an elementary analysis, to draw any conclusions about the structure and the composition of the substance. Di-p-tolyl ketone: % C 85.74, % H 6.66. Di-p-tolylacetylenylcarbinol: % C 86.48, % H 6.78, tetra-p-tolylbutinediol: % C 86.09; % H 6.72.

For the carbinol we obtained, we determined the molecular weight, which corresponded to the theoretical molecular weight of di-p-tolylacetylenylcarbinol. The acetylenic alcohol was hydrogenated; it added hydrogen to the amount required for complete hydrogenation of di-p-tolylacetylenylcarbinol.

The saturated alcohol obtained, di-p-tolylethylcarbinol, was characterized by comparing its constants with those of the known alcohol obtained by the Grignard reaction from di-p-tolylketone and ethylmagnesium bromide. The agreement was complete.

EXPERIMENTAL

The Synthesis of Methylnonylacetylenylcarbinol

In a three-necked jar, fitted with a powerful propeller stirrer, a dropping funnel, and a reflux condenser, there were placed 100 g of powdered KOH and 400 ml of absolute ether. The ether was saturated with acetylene at 0°, and

there was then added to the reaction mixture over a period of 8 hours a solution of 10 g of methylnonylketone in 150 ml of ether.

All during the experiment, a strong current of acetylene was passed through the jar. After the addition of all the ketone, the acetylene was passed through for an additional two hours. On the following day, the alcoholate was decomposed with water and the ether solution was dried over calcined potash. The ether was then driven off and the residue distilled in vacuum.

1) B.p. 115-118° at 7 mm; 2 g of ketone; 2) b.p. 119-120° at 7 mm; 4.35 g; 3) residue 2.2 g of glycol.

The second fraction corresponded to methylnonylacetylenylcarbinol. The yield of carbinol was 35%.

n_{α}^{23} 1.4484; d_4^{23} 0.8404; d_4^0 0.8583; MR_{α} 61.9.
$C_{13}H_{24}O$. Computed: MR_{α} 61.43.

The Synthesis of Di-p-tolylketone (4,4'-Dimethylbenzophenone)

In a half-liter round bottomed three-necked flask fitted with a mechanical stirrer, a dropping funnel, a thermometer, and a reflux condenser, there were placed 90 g of anhydrous aluminum chloride and 140 ml of dry carbon tetrachloride. The reaction mixture was cooled to 10-5°, and 142 ml of toluene in 140 ml of carbon tetrachloride added. The addition of the toluene took place at such speed that the temperature did not rise above 15°. When the flask was cooled with ice-water, the addition of the toluene could be completed in 40 to 50 minutes. After all the toluene had been added, stirring was continued for 5 to 6 hours more, and the reaction mixture was then poured on ice.

The excess of carbon tetrachloride was distilled off with steam. At the same time, the hydrolysis of the ditolyldichloromethane to give the corresponding ketone took place. The latter was extracted with benzene, and the mixture of ketones was distilled directly from a Wurtz flask. B.p. 320-325°.

The distillate was a mixture of three ketones: 4,4'-dimethylbenzophenone, 2,4'-dimethylbenzophenone, and 2,2'-dimethylbenzophenone. The crystalline para isomer was filtered off with suction on a porous plate and recrystallized from ethyl alcohol. After a second recrystallization, the di-p-tolyl ketone melted at 93-95°. Yield of crude product, 23%. Yield of ketone with m.p. 93-95°, 15%.

The Synthesis of Di-p-tolylacetylenylcarbinol

a) In a three-necked jar fitted with a powerful propeller stirrer there was placed 30 g of powdered caustic potash in 120 ml of ether. While acetylene was passed continuously into the reaction mixture, 4 g of the ditolyl ketone was added in 130 ml of ether. The passage of acetylene was continued for 8 hours. On the following day, water was added to the reaction vessel. The ether solution was almost colorless, and no tarring was observed during the reaction. After the ether had been distilled off, the residue, a thick oil, began to crystallize at 0°. 4 g of crude crystals were obtained. After recrystallization from petroleum ether the product melted at 85-87°. A mixed test with the ketone melted at 56°. After a second recrystallization from aqueous methyl alcohol, the product melted at 86-87°. The reaction with an ammoniacal alcoholic solution of silver oxide was positive.

0.1260 g substance: 0.3982 g CO_2; 0.0765 g H_2O.
Found %: C 86.21; H 6.78.
$C_{17}H_{16}O$. Computed %: C 86.48; H 6.78.

0.0823 g substance: 12.9 g benzene: Δt 0.14.
0.1100 g substance: 12.28 g benzene: Δt 0.2
Found: M 236.6, 232.
$C_{17}H_{16}O$. Computed: M 236.

b) As in the first experiment we obtained no γ-acetylenic glycol, we carried out a special experiment in which we arranged for the conditions which would favor its formation: 1) slow mixing of the reaction mixture, 2) a gentle current of acetylene, 3) all the ketone added at once to the reaction mixture. For the reaction we used 3.5 g of ketone, 20 g of KOH, 120 ml of ether. Acetylene was passed through for 8 hours.

On the following day, water was added to the flask. The ether layer was separated, dried over potash, and the ether driven off. The residue of 3 g began to crystallize at 0°. The product obtained was heated with petroleum ether. The insoluble part was recrystallized from aqueous methyl alcohol.

The melting point of the crystals was 152-153°. About 0.1 g was obtained. A mixed test with the glycol obtained by the method of T.I.Temnikova [4] gave no melting point depression. The compound which was dissolved in petroleum ether was separated and recrystallized from aqueous methyl alcohol. M.p. 86-87°. A mixed test with the ketone gave a melting point of 56-57°.

The Catalytic Hydrogenation of the Substance with m.p. 86-87°

The hydrogenation was carried out in alcoholic solution; 0.9 g of the substance with m.p. 86-87° was used in 100 ml of alcohol and 0.25 g of platinum black. The hydrogenation was complete after 35 minutes. A total of 186 ml of H_2 (0°, 760 mm) was added, an amount which corresponded to 109% of the theoretical amount needed for di-p-tolylacetylenylcarbinol, $C_{17}H_{16}O$.

After long standing, there precipitated out of the aqueous alcoholic solution 0.8 g of crystals, which, after recrystallization from petroleum ether, melted at 42-43°.

A mixed test with a known preparation of di-p-tolylethylcarbinol gave no melting point depression. Therefore, the substance with m.p. 86-87° actually was the tertiary acetylenic alcohol – di-p-tolylacetylenylcarbinol.

The Synthesis of Di-p-tolylethylcarbinol

To a Grignard solution prepared from 6 g of Mg and 27 g of ethyl bromide, there was added 10 g of crystalline di-p-tolyl ketone. After the addition of the ketone, the reaction mixture was heated on the water bath to 30° for 3 hours. The di-p-tolylethylcarbinol, recrystallized twice from petroleum ether, melted at 42-43°.

0.1380 g substance: 0.4303 g CO_2; 0.1025 g H_2O.
0.1000 g substance: 0.3127 g CO_2; 0.0765 g H_2O.
Found %: C 84.97, 85.28; H 8.57, 8.55.
$C_{17}H_{20}O$. Computed %: C 85.00; H 8.33.
0.0970 g substance: 18.61 g benzene: Δt 0.11°.
Found: M 245.
$C_{17}H_{20}O$. Computed: M 240.
0.0953 g substance: 6.8 ml CH_4 (0°, 760 mm).
0.0986 g substance: 9.8 ml CH_4 (0°, 760 mm).
Found: Active H atoms 0.97, 1.06.
$C_{17}H_{19}OH$. Computed: Active H atoms 1.00.

SUMMARY

1. It has been shown that di-p-tolyl ketone easily condenses with acetylene

under the conditions of the Favorsky reaction.

2. The tertiary acetylenic alcohol di-p-tolylacetylenylcarbinol is obtained.

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SYNTHESES USING ACRYLIC ACID NITRILE

IX. THE REACTION OF ACRYLONITRILE WITH AMMONIA AND THE PREPARATION OF TRIMETHYLENEDIAMINE

A. P. Terentyev, K. I. Chursina and A. N. Kost

The N. D. Zelinsky Laboratory of Organic Chemistry of Moscow State University

In the reaction of acrylonitrile with ammonia, a mixture of products is formed by mono-, di-, and tricyanoethylation:

$$NH_3 + CH_2{=}CH{-}CN \rightleftharpoons \begin{cases} NH_2CH_2CH_2CN \\ NH(CH_2CH_2CN)_2 \\ N(CH_2CH_2CN)_3 \end{cases}$$

Among these, it is the β-aminopropionitrile which is of the greatest interest. Upon saponification, it gives β-alanine, the starting point for the synthesis of pantothenic acid and its analogs, [1].

Whitmore and his coworkers [2] carried out the reaction between acrylonitrile and an aqueous solution of ammonia at room temperature and atmospheric pressure. The chief product of the reaction appeared to be β,β'-iminodipropiodinitrile, while at the same time β-aminopropionitrile was obtained in a yield of only 22%. According to the author's opinion, there was present in the system the equilibrium:

$$NH_2CH_2CH_2CN \rightleftharpoons NH(CH_2CH_2CN)_2 + NH_3.$$

At the same time, it was noted that several samples of β-aminopropionitrile polymerized upon standing. The authors assumed that in this case ammonia split off, and a polymer of acrylonitrile was obtained:

$$NH_2CH_2CH_2CN \rightleftharpoons CH_2{=}CH{-}CN + NH_3.$$
$$\downarrow$$
$$\text{polymer}$$

It was then found [3] that upon using a saturated solution of ammonia and higher pressure the yield of β-aminopropionitrile rose to 39%. Later, Ford [4] showed that at a temperature from 100 to 150°, using pressure, the reaction took place in from 2 to 5 minutes, while the yield of β-aminopropionitrile reached 92%.

Our data confirm the presence of an equilibrium in this system, in which ammonia apparently plays the chief role:

$$CH_2{=}CHCN \underset{+NH_3}{\overset{+NH_3}{\rightleftharpoons}} NH_2CH_2CH_2CN \underset{+NH_3}{\overset{-NH_3}{\rightleftharpoons}} NH(CH_2CH_2CN)_2 \underset{+NH_3}{\overset{-NH_3}{\rightleftharpoons}} N(CH_2CH_2CN)_3$$

The following reactions take place with considerably more difficulty:

$$NH_2CH_2CH_2CN + CH_2{=}CHCN \rightleftharpoons NH(CH_2CH_2CN)_2$$

$$NH(CH_2CH_2CN)_2 + CH_2{=}CHCN \rightleftharpoons N(CH_2CH_2CN)_3.$$

In fact, at a low concentration of ammonia (22%) the chief product of reaction is the tertiary aminonitrile, while raising the concentration of ammonia increases the yield of primary and secondary aminonitriles. Upon storage, pure β,β'-iminodipropiodinitrile was observed to give off ammonia, while crystals of the tertiary aminonitrile precipitated. If the samples are kept in a sealed vessel, then part of the ammonia given off enters into a reaction, and upon distillation it is possible to isolate the primary β-aminopropionitrile. In order for β,β'-iminodipropiodinitrile to decompose according to the scheme:

$$NH(CH_2CH_2CN)_2 \longrightarrow NH_2CH_2CH_2CN + CH_2{=}CHCN,$$

a temperature of above 250° is needed. The reverse process of addition of acrylonitrile to β-aminopropionitrile takes place at room temperature rather slowly, even when a large excess of acrylonitrile is used. At room temperature, β,β'-iminodipropiodinitrile practically does not react with acrylonitrile. We were able to obtain the tertiary aminonitrile with a yield of 40% only after 60 hours of heating the β,β'-iminodipropiodinitrile in a sealed ampoule at 160-180° with three times the molar quantity of acrylonitrile.

As for the polymerization of β-aminopropionitrile, our observations are opposed to the assumption of Whitmore.

We followed the polymerization of a large number of samples of β-aminopropionitrile and observed that in certain cases (without the access of air and moisture) polymerization took place almost without the evolution of ammonia. This was also confirmed by the analysis of the polymer, whose nitrogen content corresponded roughly not to that of acrylonitrile, but to that of aminonitrile. In contradistinction to the polymers of acrylonitrile, this polymer was very soluble in water.

In the catalytic reduction of β-aminopropionitrile we obtained trimethylene diamine (in a yield of 54%) and di-(γ-aminopropyl)-amine [2,5]:

$$NH_2CH_2CH_2CN \xrightarrow{[H]} \begin{cases} NH_2CH_2CH_2CH_2NH_2 \\ NH(CH_2CH_2CH_2NH_2)_2 \end{cases}$$

We carried out the reduction of β-aminopropionitrile with an alloy of sodium and potassium in normal butyl alcohol, and obtained trimethylenediamine in a yield of 80%. The formation of the secondary amine was not observed, as is usually the case in this method of reduction [6]. We obtained di-(γ-aminopropyl)-amine by the reduction of β,β'-iminodipropiodinitrile.

EXPERIMENTAL

The Reaction of Acrylonitrile with Ammonia

In a round-bottomed two-liter flask, fitted with a mechanical stirrer, a dropping funnel, and a reflux condenser, we placed 950 ml of an aqueous solution of ammonia which had been saturated in the cold (about 32%, 18 moles). Then 95 g (1.8 moles) of acrylonitrile were added drop by drop, with stirring and cooling. The operation required about 2 hours, the velocity of addition being regulated in such fashion that no second layer was formed and the temperature did not rise above 35°. The reaction mixture was then stirred for 30 minutes more at room temperature and the water driven off with the aid of a water pump. The residue was subjected to fractional distillation in vacuum, to give 37.5 g (30% of theory) of β-aminopropionitrile and 52 g (47.2% of theory) of β,β'-iminodipropionitrile. There remained in the distillation flask 3 to 5 g of very viscous reddish-brown material, which was very soluble in water. By careful precipitation from mixtures of water, alcohol, and ether, it was possible to isolate crystals of β,β', β"-tricyanotriethylamine (m.p. 57-58°).

During several repetitions of the experiments, we noted that with a smaller volume of ammonia (7 volumes) the yield of β-aminopropionitrile fell to 26%. When we used a 22% solution of ammonia (8 to 10 volumes) the yield of β-aminopropionitrile did not exceed 5%, while that of β,β'-iminodipropiodinitrile was 15%. At the same time a considerable amount of polymer was formed. If the reaction was carried out under the conditions described above, but the distillation of the water and of the β-aminopropionitrile was carried out in a current of ammonia, the yield of β-aminopropionitrile rose to 34 or 36%. If the distillation of pure β,β'-iminodipropionitrile was carried out in a current of ammonia at low pressure, then, after fractionation in a current of nitrogen, 6 to 8% of β-aminopropionitrile was obtained.

β-Aminopropionitrile is a colorless liquid. B.p. 77-78° at 14 mm; 84-86° at 18 mm; 89° at 23 mm.

n_D^{20} 1.4390; d_4^{20} 0.9584; MR_D 19.23. $C_3H_6N_2$. Computed MR_D 19.31.

Literature data: b.p. 66-69° at 5 mm [2]; 79-81° at 16 mm [3]; n_D^{20} 1.4396 [2].

The hydrochloride crystallized from ethyl alcohol as platelets with m.p. 163-163.5°. It was soluble in water and in methyl and ethyl alcohols, but insoluble in ether.

0.330 mg substance: 1.01234 ml N_2 (30°, 754 mm).
Found %: N 26.56.
$C_3H_7N_2Cl$. Computed %: N 26.29.

β,β'-Iminodipropiodinitrile (or β,β'-dicyanodiethylamine) is a viscous, colorless liquid, which becomes opalescent after standing for a short time in contact with air. It is very soluble in water and alcohol, insoluble in ether. B.p. 177-179° at 14 mm; 209-211° at 22 mm.

n_D^{20} 1.4630; d_4^{20} 1.0196; MR_D 33.25. $C_6H_8N_3$. Computed: MR_D 33.22.

Literature data: b.p. 165° at 4 mm; n_D^{20} 1.4640 [3].

The hydrochloride crystallized from methyl alcohols as needles with m.p. 147-148°. It was very soluble in water, not so soluble in alcohol, insoluble in benzene, ether, n-pentane, acetone, and chloroform.

4.117 mg substance: 0.97020 ml N_2 (29°, 753 mm).
Found %: N 26.87.
$C_6H_{10}N_3Cl$. Computed %: N 26.33.

N,N-Di(β-cyanoethyl)-benzamide – $C_6H_5CON(CH_2CH_2CN)_2$. This was obtained by the slow addition of an ethereal solution of benzoyl chloride to twice the molar quantity of β,β'-iminodipropiodinitrile. The hydrochloride of the iminonitrile was saponified with water, and the dicyanoethylbenzamide recrystallized from methyl alcohol. It was in the form of colorless needles with m.p. 112°, insoluble in water, soluble in methyl and ethyl alcohols.

0.4050 mg substance: 0.655 ml N_2 (21°, 749 mm).
0.4500 mg substance: 0.730 ml N_2 (21°, 749 mm).
Found %: N 18.51, 18.56.
$C_{13}H_{13}ON_3$. Computed %: N 18.50.

N,N-Di-(β-cyanoethyl)-benzosulfamide – $C_6H_5SO_2N(CH_2CH_2CN)_2$

This was obtained by the action of benzosulfochloride on β,β'-iminodipropiodinitrile. It crystallized from methyl alcohol as needles with m.p. 88°. It was very soluble in alcohol, slightly soluble in hot water, insoluble in ether.

0.6480 mg substance: 0.899 ml N_2 (22°, 748 mm).
Found %: N 15.76.
$C_{12}H_{13}O_2N_3S$. Computed %: N 15.96.

The Preparation of β,β',β''-Tricyanotriethylamine

A mixture of 6.2 g (0.05 mole) of β,β'-dicyanodiethylamine and 8.0 g (0.15 mole) of acrylonitrile was heated for 60 hours in a sealed ampoule at 160-180°. The reaction mixture was transformed into a red, viscous mass. The excess of acrylonitrile was distilled off, with the use of an air-pump to produce a vacuum, and the unreacted iminonitrile was carefully saponified with small portions of ice water. The residue, a dark-red viscous mass, was recrystallized from a mixture of alcohol, ether, and water. 3.5 g of colorless crystals (i.e., 40% of theory) were obtained, with m.p. 57-58°. The literature gives the m.p. as 59°[8].

The Preparation of Trimethylenediamine

In a round-bottomed flask of 1.5 ml capacity, fitted with a horn-shaped adapter and a long copper reflux condenser, there was placed 30 g of sodium-potassium alloy (98% of technical sodium plus 2% of potassium), and a solution of 14 g (0.2 mole) of freshly distilled β-aminopropionitrile in 450 ml of dry butyl alcohol was quickly added. This was at once placed in a hot (130-140°) oil bath and heated until the metal had completely dissolved. This required 40 to 50 minutes. After cooling, 150-170 ml of cold water was added to decompose the alcoholate, and the butyl alcohol and diamine were distilled off with steam (over a period of 4 to 6 hours) into a receiver containing a solution of hydrochloric acid. The alcoholic layer was separated and washed three times with a dilute solution of hydrochloric acid. The united aqueous extracts were concentrated on the water bath until crystallization began. We obtained 23 g (or 81% of theory) of the hydrochloride of trimethylenediamine, with m.p. 236°. After recrystallization from alcohol, the m.p. was 242°. The literature gives the m.p. as 240° [7] and 243° [8]. To obtain a good yield, it is necessary to use freshly prepared β-aminopropionitrile. If the preparation has stood for from 5 to 8 days, the yield falls to 65 or 70%. Upon reduction in isoamyl alcohol, trimethylenediamine was obtained in a yield of 69%.

In order to obtain the free base, 29 g of the crude trimethylenediamine hydrochloride was placed in a beaker, 10 ml of water added, and 20 to 30 ml of ether. Then, as the beaker was strongly cooled, the hydrochloride was decomposed by the addition of crushed caustic soda until a viscous mass was formed. The layer of oil which separated was extracted 8 to 10 times with ether, and the ether extract dried first with fused caustic soda, then with metallic sodium. The ether was then driven off over sodium, and the trimethylenediamine distilled, the fraction in the interval 136-138° at 756 mm being collected. The viscous residue from the extraction was placed in a copper flask and the aqueous trimethylenediamine distilled to dryness. The distillate was dried over small portions of metallic sodium under a layer of ether. The ether was driven off and the residue extracted 5 or 6 times with ether. The combined extracts were dried with metallic sodium and distilled to give a second portion of trimethylenediamine (about 4 g). Both portions were combined and again distilled, the fraction boiling at 136-138° at 756 mm or 134-136° at 735 mm being collected. 11 g of trimethylenediamine, or 74.3% of theory, was obtained, basing the calculation on the hydrochloride used.

n_D^{20} 1.4590; d_4^{20} 0.8834; MR_D 22.90. $C_3H_{10}N_2$. Computed: MR_D 22.91.

Literature data: b.p. 48-50° at 20 mm [9]; 133° at 754.5 mm [9]; 135-136° at 738 mm [8]; 131° at 760 mm [10] n_D^{20} 1.4600 [2]; d_4^{25} 0.884 [11].

We carried out experiments on the dehydration of the trimethylenediamine

over sodium or barium oxides, but in these cases the yield was considerably lower (35 to 45%).

The Preparation of Di-(γ-aminopropyl)-amine

24.6 g (0.2 mole) of freshly distilled β,β'-iminodipropiodinitrile was reduced with sodium-potassium alloy (30 g) in n-butyl alcohol medium (450 ml) by the same method described for β-aminopropionitrile. After the alcoholate had been decomposed with water, the butyl alcohol was distilled off along with the triamine by distilling with steam for 12 hours. Concentration of the acid aqueous solution gave 28 g (56% of theory) of the crude hydrochloride. The hydrochloride was decomposed by grinding with solid alkali under a layer of ether, and extracting repeatedly with absolute ether. The ether extract was dried over sodium oxide, the ether distilled off, and the triamine distilled in vacuum in a current of nitrogen. After two distillations, 7.0-7.8 g (or 23-25% of theory, based on the original β,β'-iminodipropiodinitrile) of pure di-(γ-aminopropyl)-amine was obtained. B.p. 105-106° at 5 to 6 mm; 108° at 9 mm; 114-117° at 17 mm.

n_D^{20} 1.4846; d_4^{20} 0.9386; MR_D 39.94. $C_6H_{17}N_3$. Computed: MR_D 39.42.

Literature data: B.p. 100° at 2-3 mm [2]; 128-131.5° at 20 mm [9]; 130.5° at 760.2 mm [9]; n_D^{25} 1.4802 [2]; d_4^{20} 0.9307 [2]; d_4^{25} 0.9268 [2].

The hydrochloride $C_6H_{17}N_3 \cdot 3HCl$ crystallized in the form of platelets from aqueous methyl alcohol. It melted at 259° with decomposition.

4.660 mg substance: 0.697 ml N_2 (20°, 747 mm).
Found %: N 17.13.
$C_6H_{20}N_3Cl_3$. Computed %: N 17.46.

Literature data: m.p. 254° [12].

The picrate crystallized as needles from water with m.p. 226-227° (with decomposition).

3.822 mg substance: 0.68600 ml N_2 (25°, 761 mm).
4.905 mg substance: 0.90160 ml N_2 (32°, 760 mm).
Found %: N 20.59, 20.56.
$C_6H_{17}N_3 \cdot 3C_6H_3O_7N_3$. Computed %: N 20.55.

Literature data: m.p. 230° [12].

SUMMARY

1. A study has been made of the reaction of Alkyl nitriles with ammonia; during this study, the equilibrium:

$$CH_3{=}CHCN \underset{-NH_3}{\overset{+NH_3}{\rightleftharpoons}} NH_2CH_2CH_2CN \underset{+NH_3}{\overset{-NH_3}{\rightleftharpoons}} NH(CH_2CH_2CN)_2 \underset{+NH_3}{\overset{-NH_3}{\rightleftharpoons}} N(CH_2CH_2CN)_3.$$

2. It has been found that the polymerization of β-aminopropionitrile can take place without the evolution of ammonia.

3. A laboratory method is given for the preparation of trimethylenediamine (in good yield) by the reduction of β-aminopropionitrile with sodium potassium alloy in butyl alcohol.

4. The preparation of di-(γ-aminopropyl)-amine by the reduction of β,β'-iminodipropiodinitrile has been described.

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THE USE OF KETENE AS AN ACETYLATING AGENT

I. THE QUESTION OF EXHAUSTIVE ACETYLATION OF GLYCOLS

A. A. Ponomarev and Yu. B. Isaev

Department of Organic Chemistry of the N. G. Chernishevsky Saratov State University

Because of its peculiar structure, the simplest ketene, $CH_2=C=O$, (carbonylmethylene) belongs among the most reactive substances. The ease with which ketene adds to the double bond of different compounds with mobile hydrogen atoms (alcohols, amines, etc.) makes it one of the best acetylating agents.

The valuable properties of ketene, along with its inexpensiveness and the simplicity of its preparation (by the pyrolysis of acetone) have opened a broad path for it in industry. At present ketene is made industrially on a large scale.

There is a great deal of literature about the reactions of ketene, thoroughly reviewed for us in the well-known article by A.Ya.Yakubovich [1]. Among the numerous investigations of ketene, its reactions with polyatomic alcohols and in particular with the glycols have received relatively little attention. There are well known investigations with regard to the acetylation by the use of ketene of ethylene glycols, glycerine, cellulose, and a few other hydrocarbons [2,3,4,5].

In all the cases of acetylation of ethylene glycol and glycerine, the products of reaction were mixtures of acetates. The completely acetylated compounds were not obtained as the chief products of reaction even upon the addition of such a catalyst as H_2SO_4. These, however, were of considerable interest industrially. This stimulated us to carry out a number of experiments on the acetylation by means of ketene of several glycols and aminoalcohols, in order to seek the conditions necessary for obtaining high yields of the completely acetylated compounds without considerable amounts of the other compounds. For this purpose we investigated diethylene glycol, triethylene glycol, thioglycol, and finally, monoethanolamine.

In the absence of catalysts, the acetylation of these glycols, as well as of ethylene glycol and hexenediol, actually did not go beyond the formation of mixtures of the partially and fully acetylated compounds. Tetramethylbutenediol, under these conditions, practically did not react with ketene. However, we were able to determine that several substances which were added, such as sodium acetate, were excellent catalysts for the acetylation of glycols, and that in their presence it was possible to obtain acetates in a yield up to 87% of the theoretical.

Equally deserving of attention was the fact that under different conditions, monoethanolamine, under the action of ketene, could form either the monoacetate (the N-derivative) or the diacetate as chief product.

EXPERIMENTAL*

Ketene was obtained by the pyrolysis of acetone in an apparatus of special

*The students A. G. Shilova and V. T. Kashirina assisted us in the experimental work.

construction, which allowed the recycling of the unreacted acetone. In carrying out acetylations, the ketene was bubbled through the substance to be acetylated, the latter being placed in a reaction vessel with a thermometer submerged in the liquid in order to control the course of the reaction. The end of the reaction was determined by a lowering of the temperature to its initial value. The ester number of the products of reaction was determined by the general method with an alcoholic solution of KOH, followed by titration with 0.5 N H_2SO_4 in the presence of phenolphthalein.

I. The acetylation of ethylene glycol. 12.50 g of chemically pure ethylene glycol with a n_D^{19} 1.4299 was used in the reaction. The maximum temperature during the acetylation was attained in the 130th minute (85°). Weight absorbed, 11.9 g. The results of the distillation of the products of the reaction (23.36 g) at atmospheric pressure are given in Table 1.

TABLE 1

No. of expt.	Boiling range (°)	Weight (g)	Ester number	
			Found	Computed
1	To 100°	2.05	–	Monoacetate 539.21
2	181-185	17.45	656.11, 652.10	Diacetate 767.75
3	185-192	2.80	641.74	

The data obtained permit us to conclude that the chief fraction consisted of a mixture of equal amounts of the mono- and di-acetates of ethylene glycol.

II. The acetylation of diethylene glycol. Chemically pure glycol was used, with a $n_D^{23.8}$ 1.4460.

First experiment. 18.10 g of diethylene glycol were acetylated without catalyst. The maximum temperature of 75° was observed after 1.5 hours. Weight absorbed 8.17 g. The results of a fractional vacuum distillation (at 15.5 mm) of 21.55 g of the product are listed in Table 2.

TABLE 2

Expt. No.	Boiling range, °	Weight, g	$n_D^{20.5}$	Ester number found	Percent of hydroxyl groups acetylated	Ester no. computed
1	To 134°	0.68	1.4204	–	–	Diacetate 589.93
2	136.5-141.5	13.65	1.4350	358.99 359.71	60.80	Monoacetate 378.67
3	141.5-142	1.80	1.4365	341.51	57.80	
4	142-146	2.10	1.4371	319.91	54.20	
5	146 and higher	1.27	1.4392	286.06	48.40	
	Residue	0.20	1.4467			

The hydroxyl groups acetylated were 47.77% of theory.

Second experiment. 15.00 g of diethylene glycol was acetylated in the presence of sodium acetate. The maximum temperature of the reaction mixture after 1.5 hours was 63°. The color was dark brown. Weight gained 12.80. The results of a fractional vacuum-distillation of 24.51 g of product are given in Table 3.

Analysis of fraction 3 (137.5-140° at 16 mm):

0.1226 g substance: 0.2252 g CO_2; 0.0850 g H_2O.
Found %: C 50.13; H 7.76.
$C_8H_{14}O_5$. Computed %: C 50.51; H 7.42.

TABLE 3

Fraction No.	Boiling range (°) at 16 mm	Weight (g)	n_D^{22}	Ester No. found	Percent of hydroxyl groups acetylated
1	To 131°	1.99	1.4209	–	–
2	131-137.5	4.01	1.4291	567.10 572.79	90.40
3	137.5-140	16.05	1.4300	593.00 590.00	100
4	140-148	1.07	1.4300	590.10	100
	Residue	1.00			

Yield of diethylene glycol diacetate 85.45% of theory.

III. The acetylation of thiodiglycol. Thiodiglycol had $n_D^{29.5}$ 1.5200 and b.p. 136-137° at 4 mm.

First experiment. 15.00 g of thiodiglycol were acetylated without added catalyst. The maximum temperature of the reaction mixture after 2 hours was 60°. The reaction mixture was transparent, and became slightly yellowish. Weight gained, 7.33 g. The results of a vacuum-distillation of 21.72 g of the product are given in Table 4.

TABLE 4

Fraction No.	Boiling range (°) at 7 mm	Weight, g	n_D^{29}	Ester No., found	Percent of hydroxyl groups acetylated	Ester number computed
1	143-144°	0.364	1.4811	382.42	70.10	Diacetate 545.00
2	144-145	6.24	1.4820	363.14	66.50	Mono-
3	145-147	6.89	1.4838	341.93	62.80	acetate 341.20
4	147-150	2.10	1.4861	308.30		
	Residue	1.38	1.4988			

The hydroxyl groups acetylated were 40.27% of theory.

Second experiment. 10.92 g of thiodiglycol was acetylated in the presence of 0.27 g of sodium acetate. The maximum temperature of the reaction mixture after 17 minutes was 97.5°. The color was dark brown. Weight gained, 11.68 g. The results of a fractional vacuum distillation of 22.20 g of product are given in Table 5.

TABLE 5

Fraction No.	Boiling range, (°)	Weight, g	$n_D^{29.5}$	Ester number found	Percent of di-acetate content
1	139-144°	10.47	1.4642	562.50, 563.00	100
2	144-146	3.80	1.4650	550.30	100
3	146-147	1.80	1.4650	555.94	100
	Residue	2.88			

Analysis of Fraction 1 (139-144° at 6.5 mm)

0.1006 g substance: 0.1705 g CO_2; 0.061 g H_2O.
Found %: C 46.42; H 6.80.
$C_8H_{14}O_4S$. Computed %: C 46.57; H 6.84.
$C_8H_{12}O_3S$. Computed %: C 43.87; H 7.36.
$C_4H_{10}O_2S$. Computed %: C 39.30; H 8.22.

The yield of thiodiglycol diacetate was 87.61% of theory.

IV. The acetylation of triethylene glycol. We used triethylene glycol obtained by the action of ethylene oxide on diethylene glycol in the presence of one-half of one percent of H_2SO_4. B.p. 154-156° at 6 mm; $n_D^{25.5}$ 1.4530

0.1554 g substance: 0.2736 g CO_2; 0.1308 g H_2O.
Found %: C 48.05; H 9.42.
$C_8H_{14}O_4$. Computed %: C 48.00; H 9.40.

8.72 g of triethylene glycol was acetylated in the presence of 0.2 g of sodium acetate. The maximum temperature of 74.5° was observed during the 38th minute. Weight gained, 6.58 g. The diacetate of triethylene glycol was distilled off under vacuum. B.p. 158-166° at 6 mm. Yield 10.44 g, or 80.44% of theory.

0.0752 g substance: 0.1416 g CO_2; 0.0516 g H_2O.
0.1210 g substance: 0.2286 g CO_2; 0.0850 g H_2O.
Found %: C 51.38, 51.56; H 7.86, 7.89.
$C_{10}H_{18}O_6$. Computed %: C 51.27; H 7.75.

V. The acetylation of hexine-3-diol-2,5. Hexinediol was prepared by the method of Iotsich [6]. B.p. 126-127° at 16 mm; n_D^{13} 1.4711. The substance gave a positive reaction for an acetylene glycol upon heating with solid KOH.

0.1648 g substance: 0.3820 g CO_2; 0.1368 g H_2O.
Found %: C 63.25; H 9.29.
$C_6H_{10}O_2$. Computed %: C 63.13; H 8.83.

8.01 g of hexinediol was acetylated without any added catalyst. The maximum temperature of 63° was observed in the 60th minute. Weight gained, 6.09 g. The results of a fractional vacuum-distillation of 13.95 g of product are given in Table 6.

TABLE 6

Fraction No.	Boiling range,(°)	Weight, g	n_D^{25}	Ester No. found	Percent of hydroxyl groups acetylated	Ester number, computed
1	70-112°	0.35	1.3995	-	-	
2	112-129	0.10	1.4076	-	-	
3	129-133	0.67	1.4430	-	-	
4	133-135	10.11	1.4470	443.67, 446.35, 448.18	78.90	Diacetate 566.21
	Residue	0.35				

The chief fraction analyzed as follows:

0.1788 g substance: 0.3962 g CO_2; 0.1226 g H_2O.
Found %: C 60.47; H 7.67.
$C_{10}H_{14}O_4$. Computed %: C 60.59; H 7.12.
$C_8H_{12}O_3$. Computed %: C 61.52; H 7.74.
$C_6H_{10}O_2$. Computed %: C 63.13; H 8.83.

From the results obtained, it follows that under the conditions of the experiment there was formed a mixture of mono- and di-acetates of hexinediol, which was difficult to separate by distillation.

VI. The acetylation of tetramethylbutinediol. Tetramethylbutinediol was prepared by the method of Iotsich [7]. 12 g of the compound was acetylated in liquid form without any added catalyst for 2 hours. No gain in weight of the substance used was observed. The m.p. of the product was substantially unchanged.

VII. The acetylation of monoethanolamine. The monoethanolamine used had a b.p. of 168-172 and n_D^{20} 1.4525.

First experiment. 15.00 g of monoethanolamine was acetylated in the presence of 0.2 g of sodium acetate. The color of the reaction mixture was dark brown. Gain in weight, 29.80 g. 37.80 g of the reaction mixture was subjected to vacuum distillation. The chief fraction went over at 154-174° at 24 mm. Yield 25.60 g.

n_D^{24} 1.4511; d_4^{24} 1.1015; MR_D 35.410. $C_5H_{11}O_3N$. Computed: MR_D 35.175.

0.0868 g substance: 0.1487 g CO_2; 0.0710 g H_2O.
0.1564 g substance: 0.2858 g CO_2; 0.1052 g H_2O.
Found %: C 50.35, 49.87; H 7.47, 7.53.
$C_5H_{11}O_3N$. Computed %: C 49.64; H 7.64.
0.1435 g substance: 12.3 ml N_2 (21°, 767 mm).
0.1429 g substance: 12.0 ml N_2 (23°, 768 mm).
Found %: N 9.85, 9.84.
$C_5H_{11}O_3N$. Computed %: N 9.65.

Second experiment. 10.00 g of monoethanolamine was acetylated in the presence of 0.2 g of potassium bisulfate. Gain in weight 13.92 g. 23.04 g of the reaction mixture was vacuum distilled. The chief fraction went over at 147-154° at 8 mm. Yield 13.00 g.

n_D^{21} 1.4554; d_4^{21} 1.1017; MR_D 35.661. $C_5H_{11}O_3N$. Computed MR_D 35.175.

0.1490 g substance: 13.2 ml N_2 (25°, 759 mm).
Found %: N 9.88.
$C_5H_{11}O_3N$. Computed %: N 9.65.

The results of the investigation of the substance obtained in the first and second experiments, as given above, permit us to draw the conclusion that during the acetylation of monoethanolamine with ketene under the indicated conditions the diacetate of monoethanolamine-($CH_3CONHCH_2CH_2OCOCH_3$) – β-acetoxy-N-acetylethylamine, was formed, in yields 71.90 and 58.10% of theory, respectively.

The diacetate of monoethanolamine obtained was a viscous, slightly yellowish liquid, soluble in many organic solvents and in water, insoluble in benzene, slightly soluble in ether.

When monoethanolamine was acetylated in the absence of catalyst, it was impossible to isolate the above product.

Third experiment. An aqueous solution of monoethanolamine (10.00 g of monoethanolamine per 10 g of water) was subjected to acetylation with ketene. The end of the reaction was determined when the gain in weight equalled 10.8 g. Acetone was distilled from the products of the reaction at atmospheric pressure. Water was driven off under vacuum on a boiling water bath, and the residue, without any supplementary drying, was subjected to vacuum distillation. The chief fraction went over at 166-167° (8 mm). Weight 13.76 g.

n_D^{24} 1.4703; d_4^{24} 1.1079; MR_D 25.951. $C_4H_9O_2N$. Computed: MR_D 25.910.

0.1101 g substance: 0.1906 g CO_2; 0.0906 g H_2O.
0.0868 g substance: 0.1487 g CO_2; 0.0710 g H_2O.
Found %: C 47.11, 46.75; H 9.18, 9.15.
$C_4H_9O_2N$. Computed %: C 46.85; H 8.79.
0.1273 g substance: 16 ml N_2 (26°, 765 mm).
Found %: N 13.87.
$C_4H_9O_2N$. Computed %: N 13.58.

The results of the investigation of the substance obtained in the third experiment, as listed above, permit us to draw the conclusion that the acetylation of monoethanolamine in aqueous solution with ketene gives the monoacetate of monoethanolamine ($CH_3CONHCH_2CH_2OH$) – N-acetylaminoethanol, in a yield 81.40% of theory.

The monoacetate of monoethanolamine is a viscous, colorless liquid, without odor, miscible with water and alcohol, slightly soluble in ether.

When monoethanolamine was acetylated in the absence of water, the above product was not isolated.

SUMMARY

1. The acetylation of the following aliphatic glycols has been carried out with the use of ketene: ethylene glycol, diethylene glycol, thiodiglycol, triethylene glycol, and hexinediol. It has been found that when sodium acetate is used as a catalyst the diacetates of diethylene glycol, thiodiglycol, and triethylene glycol are obtained in yields 85.45, 87.61, and 80.44% of the theoretical.

In the absence of catalyst, the action of ketene on the glycols named results in a considerably lower degree of acetylation.

The tertiary acetylene glycol, tetramethylbutinediol, without added catalyst, under the conditions of our experiment, was practically unaffected by the ketene.

2. Methods have been developed for the acetylation of monoethanolamine with ketene, permitting the preparation in good yield of either the monoacetate of ethanolamine (the N-derivative) or the diacetyl derivative, without any considerable amount of byproduct in either case. For the first time, the mono- and di- acetates of monoethanolamine have been synthesized and their chief properties described.

3. Ketene can be used successfully in the industrial synthesis of the diacetates of polyglycols and the acetates of monoethanolamine.

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SEVERAL POLYENE KETONES OF THE FURAN SERIES

A. A. Ponomarev, Z. V. Til and V. V. Zelenkova

Department of Organic Chemistry of the N. G. Chernishevsky Saratov State University

Investigations in the field of polyene ketones of the furan series have been limited chiefly to the preparation of several of the simplest furylalkyl- and aryl ketones and compounds of the type of difurfurylideneacetone.

As a result of the work of Rohmer [1], Konig [2], and Ivanov [3], and the earlier work of Schmiedt [4] the following unsaturated aldehydes of the furan series are known: β-(α-furyl)-acrolein, 1-(α-furfurylidene)-propanal, 1-(α-furfurylidene)-butanal, 1-(α-furfurylidene)-pentanal, 1-(α-furfurylidene)-heptanal, and furylpentadieneal. The simplest ketones, furfural- and difurfural-acetone [5,6], and furylhexadieneone, were also obtained from furylacrolein and acetone [1].

Starting with furfuralacetone and furylhexadieneone, and condensing them with aromatic and furan aldehydes, many others have obtained different types of mixed ketones and ketones of the type of difurfurylideneacetone [1,2,6,9]. A number of investigations have been reported [10,13] on the condensation products of furfurol with cyclohexanol and methylcyclohexanol and with several other alicyclic ketones.

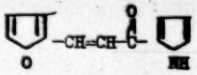
In addition to the above-mentioned furfuralacetone, difurfuralacetone, and furylhexadieneone, there are relatively few references in the literature to other unsaturated ketones obtained by the condensation of furan aldehydes with aliphatic ketones. The work done in this field has concerned chiefly the lower aliphatic ketones. Thus, Kasiwagi [14] has described furylalkyl ketones which he synthesized from furfural and methylethylketone, diethylketone and methylisopropylketone. Surmin [15] has reported the preparation of a ketone from furfurol and mesityl oxide. V.V.Chelintsev and Kuznetsova [16], and later Rudchenko, condensed furylacrolein with methylethylketone and isolated the corresponding doubly unsaturated ketone.

The condensation of furan aldehydes with acetophenone and p-methylacetophenone as well as with benzylideneacetone, was the objective of the work of a number of authors, who have reported on the unsaturated furylarylketones they obtained by this method. Thus, the corresponding ketones were obtained from acetophenone and furfurol [17,1], from acetophenone and furylacrolein [18], from p-methylacetophenone and furfurol [17,1] and from p-methylacetophenone and furylacrolein [1].

Benzylidenefurfurylideneacetone was first synthesized back in 1884 [6]. The more unsaturated ketones corresponding to it were obtained from furfuracrolein

by Rudchenko [8] in 1940.

In general, there has been little study of unsaturated ketones containing the pyrrol ring in addition to the furan ring. Thus, for example, various authors have reported on the synthesis of the ketone

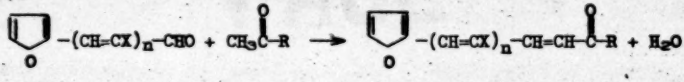


first obtained in 1917. Finzi and Vecchi [18] obtained it by condensing methylpyrrylketone with furfurol; the difurfuracrylic derivative has been obtained in an analogous manner from diacetylpyrrol. Both of these relatively little unsaturated compounds were yellow, fairly stable crystalline substances. We must note that there have also been descriptions of the condensation products of methylpyrrylketone and its homologs with benzaldehyde [20], dimethylaminobenzaldehyde [21] and several other aldehydes.

From what has been said, it follows that synthesis in the field of unsaturated furan ketones has been limited chiefly to the preparation of products with a low degree of unsaturation, such as are formed by the condensation of furfurol with various aliphatic, alkylaromatic, and heterocyclic ketones. Only a few compounds, the derivatives of furylacrolein, are known.

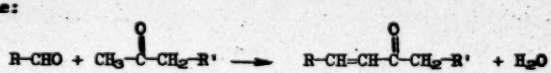
We obtained several di-, tri-, and tetraene ketones, formed by the condensation of unsaturated furan aldehydes, especially furylacrolein and furylpentadieneal, with various methylketones, including: methylisobutylketone, pinacoline, methylhexylketone, methylnonylketone, acetophenone, methylacetophenone, benzylideneacetone, and methylpyrrylketone.

In all cases, the condensation was carried out in a dilute alcohol medium under the action of a 10% solution of caustic soda, and proceeded with the formation of the corresponding polyene ketones according to the general scheme of reaction given below:



(where X = CH_3 or H; n = 1 or 2, R is the alkyl, aryl, or heterocyclic radical). The chief data about the new products are listed in Table 1; analyses in Table 2.

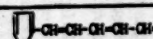
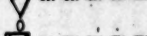
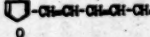
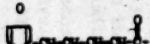
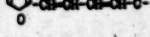
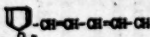
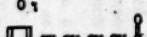
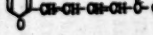
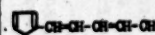
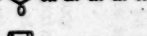
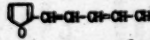
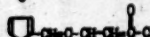
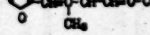
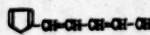
The various furylalkylketones (II, III, IV, V, VI) of normal structure listed were obtained in accordance with the numerous indications in the literature [22] of the fact that the condensation of aldehydes with methylketones under the influence of an alkaline condensing medium takes place by means of the methyl, and not the methylene group of the ketones, i.e., according to the scheme:



In complete agreement with this, for example, Scholtz and Meyer [23], in carrying out the condensation of cinnamic aldehyde with methylnonylketone under conditions analogous to ours, isolated the diene ketone of normal structure. In addition, the absence of a methyl group attached to the carbonyl in the ketones prepared by us is confirmed by the fact that not one of them gives the color reaction with sodium nitroprusside, characteristic for methylketones.

A comparison of the polyene ketones obtained by us with ketones of similar

TABLE 1

	Starting Compounds	Ketone	Yield (in % of theory based on start ketone)	Name	m.p.	m.p. of the 2,4-dinitrophenylhydrazone	Appearance	Solubility
I	Furylpentadienal and pinacoline		51	1-(α-furyl)-6,6-dimethylhexatriene-1,3,5-one-7	92°	136-137	Golden plates**	Good in hot alcohol chloroform, benzene; insoluble in water.
II	Furylpentadienal and methylisobutylketone		71	1-(α-furyl)-9-methyldecatriene-1,3,5-one-7	53	210	Orange crystals**	"
III	Furylacrolein and methylhexylketone		44	1-(α-furyl)-undecadiene-1,3,-one-5	59-60	124-125	Golden plates*	"
IV	Furylpentadienal and methylhexylketone		92	1-(α-furyl)-tridecatriene-1,3,5-one-7	78	128-129	Light yellow crystals**	"
V	Furylacrolein and methylnonylketone		45	1-(α-furyl)-tetradecadiene-1,3,-one-5	63	85-86	Orange needles**	"
VI	Furylpentadienal and methylnonylketone		90	1-(α-furyl)-hexadecatriene-1,3,5-one-7	91	111-112	Golden yellow plates**	"
VII	Furylpentadienal and acetophenone		90	1-(α-furyl)-7-phenylheptatriene-1,3,5-one-7	86-87	180	Orange needles**	"
VIII	1-(α-furfurylidene)-propanal and methylacetophenone		41	1-(α-furyl)-5-(p-tolyl)-2-methylpentadiene-1,3,-one-5	107-108	170-171	Light yellow tablets**	"
IX	Furylpentadienal and methylacetophenone		92	1-(α-furyl)-7-(p-tolyl)-heptatriene-1,3,5-one-7	119-120	184-185	Brown needles**	"
X	1-(α-furfurylidene)-propanal and benzylideneacetone		57	1-(α-furyl)-7-phenyl-2-methylheptatriene-1,3,6-one-5	99-100	~80	Yellow amorphous powder**	"
XI	Furylpentadienal and benzylideneacetone		97	1-(α-furyl)-9-phenylnonatetraene-1,3,5,8-one-7	110-111	176-177	Orange Yellow crystals**	"
XII	Furylacrolein and methylpyrrylketone		81	1-(α-furyl)-5-(α-pyrryl)-2-pentadiene-1,3,-one-5	156.5	214	Yellow tablets***	Good in hot alcohol, benzene, $CHCl_3$; slight in CCl_4; insoluble in water
XIII	1-(α-furfurylidene)-propanal and methylpyrrylketone		50	1-(α-furyl)-5-(α-pyrryl)-2-methylpentadiene-1,3,-one-5	171	225-226	Yellow scaly crystals**	Good in hot alcohol, $CHCl_3$, CCl_4, benzene; insoluble in water
XIV	Furylpentadienal and methylpyrrylketone		72	1-(α-furyl)-7-(α-pyrryl)-heptatriene-1,3,5-one-7	186	208-210	Yellow-orange scaly crystals**	Good in hot alcohol, ether, benzene; less in $CHCl_3$, CCl_4; insoluble in water

The determination of the m.p. of many 2,4-dinitrophenylhydrazones was made difficult by darkening, and a tendency to sinter before the actual m.p. was reached. ** Recrystallized from alcohol. *** Recrystallized from benzene.

TABLE 2

	Formula	Molecular weight		Elementary composition						Bromine addition (moles Br per mole ketone)
				Computed			Found			
		Computed	Found	%C	% H	%N	%C	%H	%N	
I	$C_{15}H_{18}O_2$	230.3	232.3	78.23	7.88	–	78.15	7.95	–	3
II	$C_{15}H_{18}O_2$	230.3	–	78.23	7.88	–	77.99	8.08	–	–
III	$C_{15}H_{20}O_2$	232.3	229.0	77.55	8.68	–	77.69	9.14	–	2
IV	$C_{17}H_{22}O_2$	258.5	252.2	79.04	8.57	–	79.18	8.17	–	3
V	$C_{18}H_{26}O_2$	274.4	270.9	78.79	9.55	–	78.78	9.52	–	2
VI	$C_{20}H_{28}O_2$	300.4	298.0	79.96	9.39	–	80.42	8.97	–	3
VII	$C_{17}H_{14}O_2$	250.3	253.2	81.58	5.64	–	81.17	6.1	–	3
VIII	$C_{17}H_{16}O_2$	252.3	255.4	80.92	6.39	–	81.11	6.73	–	2
IX	$C_{18}H_{16}O_2$	264.3	269.7	81.79	6.11	–	81.41	6.29	–	3
X	$C_{18}H_{16}O_2$	264.3	257.8	81.79	6.11	–	81.67	6.09	–	3
XI	$C_{19}H_{16}O_2$	276.1	280.3	82.53	5.84	–	82.27	6.1	–	–
XII	$C_{13}H_{11}O_2N$	213.2	208.5	72.75	5.2	6.57	72.45	5.35	6.88	2
XIII	$C_{14}H_{13}O_2N$	227.3	226.4	73.98	5.77	6.2	73.76	5.41	6.16	2
XIV	$C_{15}H_{13}O_2N$	239.3	244.1	75.29	5.48	5.86	75.13	5.67	6.25	– **

TABLE 3

Ketone	Concentrated H_2SO_4	Concentrated hydrochloric acid	Bromine in $CHCl_3$
VII	Green color	–	–
VIII	Cherry-red color	Weak crimson color	–
IX	Dark brown color	–	–
X	Violet, changing upon dilution with water to lemon yellow	–	–
XI	Dark cherry color	Blue green color	–
XII	Dark brown color	Crimson color	Dark red color
XIII	Dark brown color	Dark red color	Dark yellow color
XIV	Dark brown color	Clear crimson color	Dark cherry color

Note: The color arises upon the addition of particles of the substance to a few milliliters of the corresponding reagent.

structure and a lower degree of unsaturation, as reported in the literature, permits us to conclude that the regularities in the change of physical properties are completely confirmed. This is particularly true of the melting point, which changes with the increase in the molecular weight and degree of unsaturation within the limits of each series.

Furylalkylketones form soft, waxy crystals with a low melting point, the others have relatively high melting points. Several of the products obtained are distinguished by the high degree of double refraction of the crystals.

Furan ketones with aliphatic radicals (I, II, III, IV, V, VI) do not give a color reaction with concentrated H_2SO_4, hydrochloric acid, or bromine. The remaining ketones are characterized by halochroism; the ketones listed in Table 3 show various color reactions.

According to Rast, in camphor.

**Not determined, difficulty soluble in CCl_4 and $CHCl_3$.

EXPERIMENTAL

β-(α-Furyl)-acrolein was obtained by the method of König [2] from furfural and acetaldehyde. As a result of modifications in the conditions of the experiment (temperature about −3°, duration of reaction 3.5 hours) it was possible to increase the yield of furylacrolein to 72.4%, based on the original furfural.

Furylpentadieneal was also synthesized by the method of König [2]. 1-(α-furfurylidene)propanal was obtained by the method proposed by Ivanov [3], from furfural and propionic aldehyde. All the polyene ketones listed in Table 1 were obtained by condensation, using a mole to mole ratio of β-(α-furyl)acrolein, 1-(α-furfurylidene)propanal, or furylpentadieneal with the ketones in aqueous-alcoholic medium, under the influence of a 10% solution of caustic soda. The following typical experiments may serve to indicate the conditions of reaction.

The condensation of furylacrolein with methylnonylketone. To a transparent solution of 4 g of furylacrolein and 5.58 g of methylnonylketone in 25 ml of 70% ethyl alcohol, there was added drop by drop, with shaking, 4 ml of a 10% solution of NaOH. The solution first grew dark, then separated into layers, and after 30 minutes formed yellow crystals. After a day, the crystalline product was removed from the mother liquor, washed with a 2% solution of acetic acid, and then several times with water. Crystallization from pure alcohol gave large needle-shaped orange crystals with m.p. 63°; from dilute alcohol, fine crystals of a light cream color precipitated out, with the same melting point. The yield of crude product was 4 g, or 45% of the theoretical.

The preparation of the 2,4-dinitrophenylhydrazone was carried out by the general method of adding an excess of a solution of dinitrophenylhydrazine in alcohol saturated with hydrochloric acid to an alcoholic solution of the ketone at room temperature. The color of the solution very quickly changed to claret, and the precipitation of crystals of a dark claret color began. After a day the crystals were filtered off, washed with alcohol, and dried in a vacuum dessicator. M.p. 85-86°.

The condensation of furylpentadieneal and p-methylacetophenone. 3.6 g of furylpentadieneal and 3.5 g of p-methylacetophenone were dissolved in 20 ml of 85% alcohol, and to the solution there was added with shaking and in small portions, 5 ml of a 10% solution of caustic soda. After 5 minutes, the entire mass began to crystallize. In order to purify it from alkali, the product was suspended in a 2% solution of acetic acid, and then washed repeatedly with water. Recrystallization from pure alcohol gave needle-shaped crystals of brown color, with m.p. 119-120° (after two recrystallizations); from an aqueous-alcoholic solution, fine orange-colored crystals were obtained with the lower melting point of 117-118°. The yield of crude product was 4.26 g, or 92%; the yield of pure product was 3.15 g, or 68.03% of the theoretical.

The condensation of 1-(α-furfurylidene)propanal with methylpyrrylketone. To a solution of 3.26 g of methylpyrrylketone and 4.08 g of 1-(α-furfurylidene)-propanal in 30 ml of 60% alcohol there was added drop by drop 2.5 to 3.0 ml of a 10% solution of caustic soda. A change in the color of the mixture was observed, and after a day yellow crystals precipitated out. These were removed, washed on the filter with a dilute (2%) solution of acetic acid, then several times with water, and recrystallized from alcohol. The weight of the crude product was 3.44 g (50.6% of theory), of the recrystallized product 1.84 g. The twice recrystallized product had a constant m.p. of 171°.

SUMMARY

1. It has been shown that furan unsaturated aldehydes condense with alkyl, alkylaromatic, and heterocyclic methyl ketones, giving good yields of the corres-

ponding di-, tri-, and tetraene ketones.

2. A method of preparation has been given and the most important properties described for polyene ketones of the furan series, formed by the condensations of: β-(α-furyl)acrolein with methylhexylketone, methylnonylketone, and methylpyrrylketone; 1-(α-furfurylidene)propanal with p-methylacetophenone, benzylideneacetone, and methylpyrrylketone; furylpentadieneal with pinacoline, methylisobutylketone, methylhexylketone, methylnonylketone, acetophenone, p-methylacetophenone, benzylideneacetone, and methylpyrrylketone.

All the above polyene ketones have been synthesized for the first time.

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THE MECHANISM OF THE CONTACT TRANSFORMATIONS OF HYDROCARBONS ON VANADIUM CATALYST

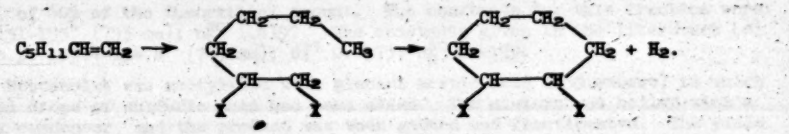
VI. THE COMPARATIVE BEHAVIOR OF HEPTENE-1 AND HEPTENE-3

A. F. Plate and G. A. Tarasova

Institute of Organic Chemistry of the Academy of Sciences of the USSR

In previous communications, on the basis of experimental results obtained, we expressed ourselves at length to the effect that the formation of aromatic compounds from alkanes took place in two ways: part of the alkanes were directly converted into aromatic compounds, while another part gave alkenes, part of which was further changed into aromatic compounds.

In this connection it was of interest to investigate the influence of the position of the double bond in the alkene on its transformation into aromatic compounds. A preliminary review of this question forced us to make two assumptions: on the one hand, in the presence of a catalyst like vanadium trioxide, in accordance with the usual picture of the mechanism of the cyclization of alkenes, only the alkenes with the double bond in the extreme position, that is, the alkenes-1, are capable of undergoing this reaction:



On the other hand, in the presence of such a catalyst, the mutual isomerization of alkenes is very probable, with the shifting of the double bond and the formation of a mixture of isomers.

There have been several investigations of the comparative aromatization of alkenes. Hoog, Verheus, and Zuiderweg [1] showed that in the presence of chromic oxide, independently of whether the original hydrocarbon was heptene-1 or heptene-2, there was heptene-3 in the product of the reaction, that is, isomerization took place with a shift of the double bond. On the basis of these data we might expect that the velocity of the cyclization of alkenes distinguishedby the different positions of the double bond would be identical. In fact, the same authors showed that heptene-1 and heptene-2 underwent ring-formation with the same velocity. This was confirmed by Taylor and Turkevich [2] with regard to heptene-1 and heptene-3. However, at the same time, Hoog, Verheus, and Zuiderweg [1] showed that in the case of hexene-1 and hexene-2 there was a considerable difference in the velocity of aromatic-formation. In the discussion which arose on this occasion [3], no attention was paid to the fact that there was an essential difference in the cyclization of heptene-2 and hexene-2; if heptene-2 is still capable of direct cyclization in the case of activated

adsorption on the catalyst because of its double bond, and in this respect does not differ essentially from heptene-1, then hexene-2 has already lost this ability and we must assume that its aromatization must take place by way of isomerization, or that it must aromatize in a manner similar to that of the saturated heptane.

In the present work, we compared the behavior of heptene-1 and heptene-3 in the presence of vanadium catalyst. Both these hydrocarbons may be comparatively easily obtained as individuals, whereas the preparation of pure heptene-2 is hampered by great difficulties. It appeared that there actually took place a mutual isomerization of both alkenes into each other and into heptene-2, the apparent values of the energy of activation of the overall dehydrogenation of both heptenes being the same. Despite this, under similar conditions, heptene-1 forms a greater amount of aromatic hydrocarbons, while in the case of heptene-3 there is a more strongly manifested tendency toward cleavage of the molecule to give hydrocarbons of lower molecular weight. This is the result of the more pronounced poisoning of the catalyst. We must draw the conclusion that heptene-1 has a greater tendency to react than heptene-3 with regard to those reactions which may be regarded as addition at the double bond (aromatization, polymerization, hydrogenation), while heptene-3 has a greater tendency to react when it comes to cleavage of the C-C bond. In the case of neither alkene did we observe isomerization accompanied by a change in the hydrocarbon skeleton.

EXPERIMENTAL

The original hydrocarbons. Heptene-1 was synthesized from n-butyl magnesium bromide and allyl chloride [4], and had the following properties: b.p. 93.5-93.6° (760 mm); d_4^{20} 0.0697; n_D^{20} 1.4000; MR_D found 34.10; computed for C_7H_{14} MR_D 34.06.

Heptene-3 was prepared by the pyrolysis of the acetate of heptanol-4, which was synthesized from n-propylmagnesium bromide and butyraldehyde [5]. The yield of the fraction corresponding to heptanol-4 consisted, after repeated fractionation, of 60% of the theoretical amount. The constants for this fraction were: b.p. 151-155° (753 mm); n_D^{20} 1.4197. The constants given in the literature [6] are: b.p. 153.4-154.4° (745 mm); d_4^{25} 0.8175; n_D^{20} 1.4199.

Heptanol-4 was acetylated with glacial acetic acid (25% excess) to which several drops of sulfuric acid had been added. The mixture was boiled with a reflux condenser, and the product was then washed and fractionated. The yield of the fraction corresponding to the acetate of heptanol-4 was 62%. Its properties were as follows: b.p. 170-172° (746 mm); d_4^{20} 0.8630; n_D^{20} 1.4100; MR_D found 45.40; computed for $C_9H_{18}O_2$ MR_D 45.42. The acetate of heptanol-4 is not described in the literature.

The pyrolysis of the acetate was carried out by the method of Wibaut and van Pelt [7] at 450°. The catalytic reaction tube was filled with glass wool. The product obtained was washed free of acetic acid, fractionated several times from a flask with a herringbone condenser, and then distilled through a column fitted with separate loops of wire with the effectiveness of 37 theoretical trays. The yield of heptene-3 amounted to 55% of the theoretical amount, based on the acetate used. It had the following properties: b.p. 95.5-95.6° (760 mm); d_4^{20} 0.6990; n_D^{20} 1.4033; MR_D found 32.43; computed for C_7H_{14}, MR_D 34.06.

For mixtures of the cis- and trans- isomers of heptene-3, the literature gives the following constants: b.p. 95.8-96.0° (760 mm); d_4^{20} 0.7010; n_D^{20} 1.4093.

The catalyst used was vanadium trioxide on aluminum oxide (1:10) [8]. Before each experiment or series of experiments, the catalyst was regenerated. After each regeneration it had exactly the same activity.

Apparatus and method of work. The experiments were carried out in a circulatory system such as has been previously described [9]. The diameter of the catalyst tube was 11 mm, the volume of catalyst 20 ml, the length of the layer 220 mm. The content of unsaturated hydrocarbons was determined by the use of bromine numbers [10]. To determine the toluene in the catalysts, the latter were hydrogenated in the cold in alcoholic solution with palladium black, and the content of toluene in the saturated product obtained was determined by the index of refraction of binary mixtures of heptane and toluene [11]. Preliminary experiments with mixtures of toluene and heptene-1 showed that under the conditions used, the toluene was not hydrogenated. However, as can be seen from Table 1, the discrepancy between the amounts of toluene taken and that found, independent of the content of the latter in the mixture, amounted to 2.3 to 2.9%. It is

TABLE 1

Expt. No.	Composition of hydrogenated mixture (in g)			Content of toluene in mixture, (mol %)	Amount of hydrogen (in ml N.T.P.)		Toluene found (mol %)	Δ
	Hepten-1	Hepten-3	Toluene		should have been absorbed	actually absorbed		
1	1.164	–	0.525	29.7	266	274	27.4	-2.3
2	0.587	0.336	0.225	19.1	211	210	16.2	-2.9
3	–	0.418	0.258	36.3	96	104	33.7	-2.6

possible that the decrease in toluene content as determined by this method may be explained by the difference in solubility of the toluene and heptane when the hydrocarbons are washed out with alcohol after hydrogenation, or by selective adsorption by the catalyst. However, if this method appears to be suitable for the determination of aromatic compounds in the catalyzed product from heptene-1, then in the case of the product from heptene-3, positive results were not obtained – the catalyzed product could not be completely hydrogenated.

Analysis of the vapor for carbon dioxide, carbon monoxide, unsaturates, hydrogen, and methane hydrocarbons was carried out in an Orsat type apparatus. The methane hydrocarbons and hydrogen were determined by combustion over copper oxide. In this case mercury was used as a sealing liquid. The amount of "coke" precipitated on the catalyst was found by determining the carbon in a sample of treated catalyst.*

The determination of the apparent energy of activation of the overall reaction of dehydrogenation and cyclization of heptene-1 and heptene-3. The method of carrying out the experiments has been previously described [12]. The experiments were carried out in the temperature range from 400 to 480°, that is, at a lower temperature than in the case of the experiments with pentane. As can be seen from Figs. 1 and 2, the amount of gas evolved was fairly uniform, and during the time of the experiment (36 minutes) the poisoning of the catalyst had little influence on the amount of gas evolved per unit of time. The results of the experiments at different temperatures with both heptenes are listed in Table 2. It was assumed that the hydrogen content of the gas changed little with the temperature [7] and therefore in considering the velocity of the reaction, we utilized the average amount of the total gas evolved in 3 minutes.

Arrhenius lines, constructed on the basis of the experimental results, were parallel in the case of both pentenes (Fig. 3). The apparent energy of activation for the dehydrogenation amounted to 39,500 cal/mol for heptene-1 and 40,000 cal/mol for heptene-3. These values are not only practically equal to each other, but also equal to the corresponding value found for n-pentane [12] (41,100 cal/mol). Fig. 3 also shows the relationship between the logarithm of

* The analysis was carried out in the Microanalysis Laboratory of the Institute of Organic Chemistry of the Academy of Sciences of the USSR.

TABLE 2

No. of Exp.	Temp. of Exp.	Velocity		Log of amount of gas evolved in 5 min.	$\frac{1}{T} \cdot 10^{-5}$	Catalysate				
		Of passage (ml/3min)	Of gas evolution (ml/3min)			n_D^{20}	Bromine No.	% unsaturates	% of unsaturates which reacted	% of aromatics
				Heptene-1 1.4000						
27^1	400°	0.75	2.87	0.458	148.6	1.4065	155.3	95.0	5.0	2.2
27^2	444	0.54	9.79	0.991	139.5	1.4090	136.9	83.8	16.2	5.0
27^4	451	0.52	13.65	1.135	138.1	1.4110	140.4	86.0	14.0	6.2
27^3	467	0.52	23.26	1.367	135.2	1.4147	128.2	78.5	21.5	9.7
27^5	480	0.51	44.85	1.652	132.8	1.4190	119.0	72.9	27.1	15.3
				Heptene-3 1.4033						
28^1	400	0.62	3.80	0.580	148.6	1.4070	144.9	88.7	11.3	Not determined
28^2	442	0.61	11.31	1.053	139.9	1.4090	132.8	81.3	18.7	
28^4	453	0.55	16.02	1.205	137.7	1.4105	125.7	77.0	23.0	
28^3	469	0.55	30.24	1.480	134.8	1.4138	119.0	72.9	27.1	

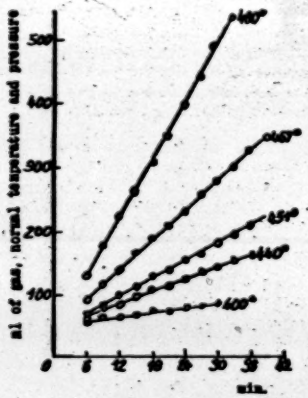


Fig. 1. Experiment 27, heptene-1.

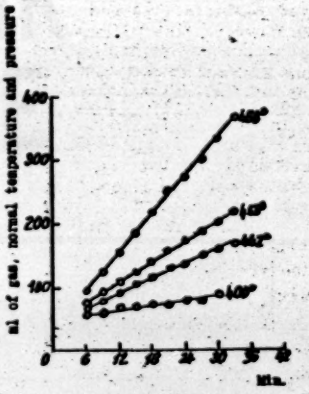


Fig. 2, Experiment 28, heptene-3.

the amount of toluene formed from heptene-1 and the reciprocal of the temperature. These data also confirm Arrhenius' equation, according to which the apparent energy of activation of the reaction for the formation of toluene from heptene-1 is equal to 33,500 cal/mol. The values obtained are considerably lower than the value of the apparent energy of activation of the reaction for the formation of toluene from heptane [12], determined by us by the same method. This was equal to 50,700 cal/mol. The values of the apparent energy of activation, Q, the coefficients of proportionality, K_0, and the coefficients of the logarithmic relationship

TABLE 3

Reaction	K_0	$\frac{Q}{\log K_0} \cdot 10^{-3}$	Q, cal/mol
Overall process of dehydrogenation of heptene-1	$2.103 \cdot 10^{13}$	2.96	39,500
Formation of toluene from heptene-1	$8.07 \cdot 10^{13}$	3.07	33,500
Overall process of dehydrogenation of heptene-3	$2.195 \cdot 10^{12}$	3.24	40,000
Overall process of dehydrogenation of heptane [12]	$1.187 \cdot 10^{13}$	3.15	41,000
Formation of toluene from heptane [12] ...	$1.107 \cdot 10^{15}$	3.37	50,700
Formation of heptene from heptane [12] ...	$5.500 \cdot 10^{5}$	3.07	17,600

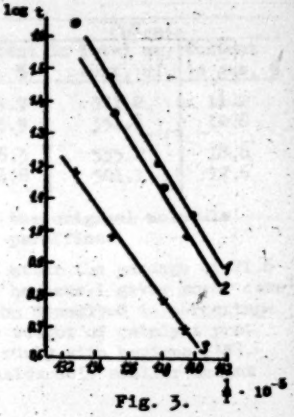


Fig. 3.

1-Expt. 28, heptene-3; 2-Expt. 27, heptene-1; 3-heptene-1 aromatic.

$\frac{Q}{\log K_0}$ are given in Table 3.

Judging from the indices of refraction of the catalyst products obtained at the same temperature, heptene-1 gives more toluene than heptene-3, (the difference between the indices of refraction of the catalyst product and the original hydrocarbon is greater in the case of heptene-1). This is quantitatively confirmed by the following experiments.

Comparative experiments on the cyclization of heptene-1 and heptene-3 at 480°. The experiments with both hydrocarbons were carried out under strictly uniform conditions: temperature 480°, duration of experiment 3 hours, amount of hydrocarbon passed through 21.6 g. The results of the experiments are given in Table 4. Apparently, heptene-3 poisons the catalyst more quickly than heptene-1,

TABLE 4

Duration of Expt.	Velocity: passage of gas (ml/hr.)	Velocity: evolution of gas (ml/hr.)	Total evolution of gas from beginning of Expt. in ml.	n_D^{20} of catalyzate	Hydrocarbon passed through, g	Catalyzate obtained, g	Yield of catalyzate in %
Experiment 29. Heptene-1				1.4000	–	–	–
1st hr.	10.2	1119	1119	1.4250			
2nd hr.	10.2	1114	2233	1.4240	21.6	19.2	88.9
3rd hr.	10.0	1082	3315	1.4225			
Experiment 30. Heptene-3				1.4033			
1st hr.	9.4	974	974	1.4240			
2nd hr.	10.7	928	1902	1.4200	21.7	19.3	88.9
3rd hr.	10.0	945	2847	1.4193			

as can to some extent be deduced from the fall in the value of the index of refraction of the catalyzate.

An analysis of the gas (Table 5) shows that the heptenes give gases of different compositions. In the case of heptene-1, the gas is richer in hydrogen,

TABLE 5

Expt. No.	Original hydrocarbon	C_nH_{2n}		H_2		C_nH_{2n+2}	
		Total amount, ml	Content in gas, %	Total amount, ml	Content in gas, %	Total amount, ml	Content in gas, %
29	Heptene-1	139.2	4.2	2807.8	84.7	371.2	11.2
		116.0	3.5	2847.6	85.9	351.4	10.6
30	Heptene-3	165.1	5.8	2172.3	76.3	535.2	18.8
			5.8	2186.5	76.8	501.1	17.6

and in the case of heptene-3, a greater destruction of the original molecule takes place, with the formation of gaseous olefins and paraffins.

Analysis of the "coke" deposited on the catalyst after the passage of 21.6 g of hydrocarbon showed that under the same conditions heptene-1 gives more "coke" than does heptene-3. Table 6 lists the amount of carbon deposited in percentage of the weight of hydrocarbon passed through and of the weight of catalyst product. The same table lists the results obtained previously with heptene [12]. From these data it is obvious that heptane forms a considerably smaller amount of "coke" than the heptenes.

TABLE 6

Expt. No.	Original hydrocarbon	Hydrocarbon passed through, g	Coke, in weight % of hydrocarbon passed through	Coke, in weight % of catalyzate
29	Heptene-1	21.6	1.2	2.3
30	Heptene-3	21.7	0.84	1.65
-	Heptane [12]	5.3	0.24	0.15

Inasmuch as heptene-3, as follows from an analysis of the gas to a great extent undergoes cleavage of the C–C bond, we may assume that the large amount of "coke" in the case of heptene-1 is formed not as a result of its destruction, but as the result of profound polymerization, toward which it is more inclined than heptene-3. Probably, the polymer reacts with the original hydrocarbon to undergo disproportionation of the hydrogen, as a result forming "coke" and heptane.

The catalyzates from the experiments with both olefins were investigated for their contents of aromatics and unsaturated hydrocarbons, and then distilled in a column furnished with separate wire coils, and an effectiveness of 37 theoretical trays. The distillation curve was plotted at the same time as the distillate was fractionated. The results of this investigation are shown in Tables 7 and 8. From these data it follows that the catalyst product of heptene-3 had more unreacted olefin (approximately 10%). This difference completely disappears in the heptene-heptane fraction, as the olefin content of the chief fraction and of the toluene fraction is the same for both heptenes. Less toluene was formed from heptene-3 than from heptene-1, that is, heptene-3 formed a ring less readily than heptene-1, a fact which was confirmed by the amount of hydrogen evolved in the two cases (cf. Table 5).

The distillation curves of both catalyzates are almost identical (Figs. 4 and 5), especially in the middle heptene-heptane fraction. The investigation of the heptene-heptane fractions by the method of combined light scattering * showed that whether the original hydrocarbon was heptene-1 or heptene-3, the heptene-heptane fractions of the catalyst product consisted of mixtures of heptene-

*We take this occasion to express our profound thanks to N. L. Batuyev for his optical investigations of the fractions.

TABLE 7

Catalyzate of Heptene-1

Boiling range of fraction at 760 mm	Amount of fraction		n_d^{20}	d_4^{20}	Bromine No.	% olefins		Aromatics	
	g	%				In fraction	In catalyzate	In fraction	In catalyzate
Total catalyzate	23.7	100	1.4230	0.7348	95.0	–	58.2	–	20.0 *
38.9-91.4	2.8	11.8	1.4025	–	143.2	75.2	8.9	–	–
91.4-100.0	12.9	54.4	1.4036	0.7025	113.5	69.5	37.8	–	–
106-114	4.7	19.8	1.4835	0.8396	29.9	17.2	3.4	91.2**	18.1
114-180	0.9	3.8	1.4942	uninvestigated					
Residue	0.5	2.1	–	–	–	–	–	–	–
Loss during dist.	1.9	8.0	–	–	–	–	–	–	–

TABLE 8

Catalyzate of Heptene-3

Boiling range of fraction at 760 mm	Amount of fraction		n_D^{20}	d_4^{20}	Bromine No.	% olefins		Aromatics	
	g	%				In fraction	In catalyzate	In fraction	In catalyzate
Total catalyzate	19.7	100	1.4198	0.7267	112.0	–	68.7	–	18.3 *
40.3-91.4	2.8	14.2	1.4002	0.6928	156.4	82.1	11.7	–	–
91.4-98.5	12.0	60.9	1.4037	0.7032	125.1	76.6	46.6	–	–
107-115	2.7	13.7	1.4827	0.8351	38.8	22.3	3.1	89.5**	12.3
115-170	1.0	5.1	1.4890	uninvestigated					
Residue	0.2	1.0	–	–	–	–	–	–	–
Loss during dist.	1.0	5.1	–	–	–	–	–	–	–

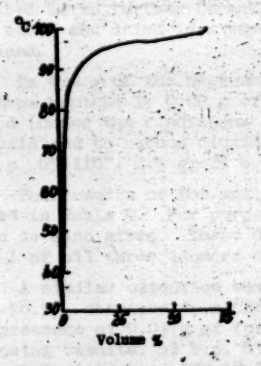


Fig. 4. Distillation curve for catalyzate of heptene-1.

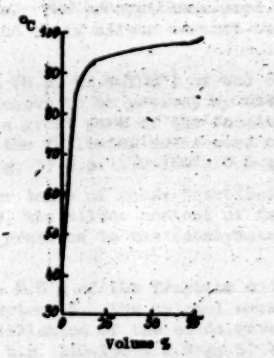


Fig. 5. Distillation curve for catalyzate of heptene-3.

*Determined from n_D after hydrogenation of catalyst product.

**Determined by the method of specific dispersion.

heptene-2, and heptene-3. Thus, along with the formation of aromatics, there took place the isomerization of the heptenes, with a shift of the double bond. If not for this isomerization, the difference in the amount of aromatics formed from heptene-1 and heptene-3 would have been greater. In order to confirm this conclusion, the heptene-heptane fractions of both catalyst products were subjected to oxidation with a neutral solution of 1% potassium permanganate. In a separate

TABLE 9

Boiling range of acid fraction	Relative order of precipitate	Percent silver in salts (found)	Possible acids	Boiling point of acid	Theoretical % of silver in salt
56-110°	–	–	Formic	100.8°	–
110-170	VI	58.1	Acetic	118	64.67
	V	57.4	Propionic	140.7	59.67
	IV	55.7	Butyric	163.5	55.38
	III	53.6	Valeric	187.0	51.67
	II	53.9			
	I	53.8			
170-180	V	53.4	Butyric	163.5	55.38
	IV	51.3	Valeric	187.0	51.67
	III	50.3	Caproic	204.2	48.43
	II	49.0			
	I	49.4			

test of the mixture of acids obtained, the formic acid was determined by the gravimetric calomel method. The greater part of the solution was concentrated and treated with sulfuric acid, and the fatty acids which separated were fractionally distilled. A qualitative analysis of these acids was carried out by the method of fractional precipitation of their silver salts, based on the differences in their solubilities.

The method of fractional precipitation of the silver salts was carried out as follows: to the acid fraction there was added a small quantity of a 5% solution of silver nitrate. The precipitate was filtered off, and the filtrate again precipitated. This was repeated until the addition of the silver nitrate resulted in no further formation of precipitate. The precipitates were washed with ether and dried in a vacuum desiccator, and their silver content then determined.

In 4.9 g of the heptene-heptane fraction (b.p. 92.4-100°) of the catalyzate from heptene-1, 0.02 g of formic acid was shown to be present by the calomel method (under the conditions of the analysis, a great part of the formic acid was oxidized to carbon dioxide). In addition the following acids were obtained: 1) b.p. 65-110°, 0.5 g; 2) b.p. 110-170°, 1.5 g; 3) b.p. 170-180°, 0.6 g.

The results of the analyses of the silver salts of these fractions are listed in Table 9. For purposes of comparison, the silver content of fatty acids is also given. These data indicate the presence in the catalyzate of heptene-1 of all three isomers of heptene.

A similar oxidation was carried out with 8.8 g of the fraction with b.p. 91.4-98.5°, obtained from the catalyzate of heptene-3. The calomel method showed the presence of 0.07 g of formic acid. A distillation of the acids gave the following results: 1) b.p. 65-110°, 1.3 g; 2) b.p. 110-150°, 2.4 g; 3) b.p. 150-170°, 1.5 g; 4) b.p. 170-185°, 1.4 g.

Analyses of the silver salts are listed in Table 10. From the data obtained, it follows that the catalyzate from heptene-3 also consisted of a mixture of the

TABLE 10

Boiling range of acid fraction	Relative order of precipitate	Percent of silver in salts (found)	Possible acids	Boiling point of acid	Theoretical % of silver in salt
110-150°	II	57.4	Propionic	140.7	59.67
	I	55.5	Butyric	163.5	55.38
150-170	III	57.3	Propionic		
	II	54.8	Butyric		
	I	52.7	Valeric	187	51.67
170-193	III	52.7	Valeric		
	II	50.5			
	I	50.1	Caproic	204.2	40.7

isomeric heptenes.

Part of the heptene-heptane fraction of the catalyzate from heptene-1 was hydrogenated in the cold with palladium black, and then investigated by the method of combined light scattering. The spectrum of the hydrogenated catalyzate corresponded to the spectrum of n-heptane. No hydrocarbons of branched structure were observed.

SUMMARY

1. Experiments with heptene-1 and heptene-3 have been carried out at temperatures from 400 to 480° in the presence of vanadium catalyst. They showed that the apparent energies of activation of the overall reactions of dehydrogenation of heptene-1 and heptene-3 were equal (39,500 cal/mol and 40,000 cal/mol), and also equal to the apparent energy of activation of the overall dehydrogenation reaction of heptane (41,100 cal/mol).

2. The apparent energy of activation for the formation of aromatics from heptene-1 equaled 33,500 cal/mol, a much lower figure than the energy of activation for the formation of aromatics from heptane (48,000 cal/mol).

3. Comparative experiments have been carried out on the formation of aromatics from heptene-1 and heptene-3 at 480°, with a volume velocity of passage of 0.5. It has been shown that under similar conditions, heptene-1 gives more aromatics than heptene-3. During the dehydrogenation and cyclization of heptene-3, the accompanying reaction of cleavage of the molecules to give low molecular weight hydrocarbons takes place to a greater extent (olefins in gas 6%, paraffins 18%), a fact which favors the more rapid poisoning of the catalyst.

4. Along with the formation of aromatics, there takes place the isomerization of the original heptenes accompanied by a shift in the double bond, forming as a result a mixture of heptene-1, heptene-2, and heptene-3. This isomerization does not favor ring formation, as heptene-3 is more inclined to give side reactions.

5. Under the conditions investigated, no isomerization of heptene-1 and heptene-3 to give a changed carbon skeleton has been observed.

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THE STRUCTURE OF THE POLYMERS OF 2,3-DICHLOROBUTADIENE-1,3 AND 1,2,3-TRICHLOROBUTADIENE-1,3

A. L. Klebansky and K. K. Chevichalova

One of the most interesting halogen derivatives of butadiene-1,3 and one of the least studied with regard to its polymerization and the properties of its polymers is 2,3-dichlorobutadiene-1,3. With regard to speed of polymerization, it stands in the first place among the butadiene derivatives now known. According to the data of Berchet and Carothers, 2,3-dichlorobutadiene-1,3 polymerized completely at room temperature in 24 hours, and in 40 minutes at 85-90°, i.e., 7 times as rapidly as chloroprene, and 7000 times as rapidly as isoprene [1]. These data were later on corrected by Carothers, and the velocity of polymerization shown to be 2000 times as great as that of isoprene [2]. According to the original data of Carothers, the polymer does not possess rubber-like properties. In their patent, these authors indicate the possibility of carrying out the polymerization of 2,3-dichlorobutadiene step by step: the monomer is first polymerized to form a plastic mass, the latter is then mixed with fillers, and polymerization is then carried further, to the end [3]. Valuable polymers can be obtained from 2,3-dichlorobutadiene-1,3, according to the data of Muller, Cunradi, Cantzler, and Daniel [4], if the monomer is made to polymerize in the presence of catalysts – peroxide compounds, especially hydrogen peroxide. The polymer is not combustible, and depending on the method and the extent of polymerization, its properties range from that of a soluble polymer to one that does not swell in different solvents. According to the data of the above authors, the polymer can be used as a synthetic, but not as a substitute for rubber.

Our experiments on the polymerization of 2,3-dichlorobutadiene-1,3 under various conditions showed that it does not form a rubber, but gives a completely thermoplastic mass, reminiscent of the properties of gutta-percha. To show the relationship of these properties of the polymers to the peculiarities of their chemical structure, the polymer was ozonized. Ozonation gave a considerable amount of formaldehyde (18.04% of the carbon skeleton of the ozonide) and formic acid (6.1%). The yield of succinic acid did not exceed 42.75% of the carbon skeleton of the ozonide of 2,3-dichlorobutadiene-1,3. The overall balance of products of the decomposition of the ozonide which were separated and determined did not exceed 67% of the carbon skeleton. As no tars or other products of decomposition were obtained, we may assume that most of the products went off under the action of excess oxygen as volatile HCl, CO_2, and CH_2O during the reaction. The formation of a large amount of formic acid and formaldehyde indicates that the links of the polymer were considerably branched, in contradistinction to the molecules of chloroprene polymer, in which the links are predominantly attached in the 1,4–1,4 arrangement.

During the synthesis of 2,3-dichlorobutadiene-1,3 from dichlorobutene, about 15 to 20% of 1,2,3-trichlorobutadiene-1,3 was formed. According to the data of Carothers, the velocity of polymerization of this compound is 1/5.8 th that of chloroprene, and 1/16.5 th the velocity of polymerization of 2,3-dichlorobutadiene-1,3. During the first stages of polymerization (up to 40%) the polymer is soluble in plasticizers, has rubber like properties, and is reminiscent of the α-polymer of chloroprene. Upon carrying the polymerization further, it becomes dense, hard, and unlike rubber; it is more like a hard plastic mass. Upon ozonation, it was found that the chief product of the decomposition of the ozonide was fumaric acid - 81.5% of the carbon skeleton. These data indicate that in the polymer of 1,2,3-trichlorobutadiene-1,3, the normal linear structure predominates.

$$-CHCl-CCl=CCl-CH_2-CHCl-CCl=CCl-CH_2-.$$

The chief polymer unit $\rangle CCl-CH_2-CHCl-CCl\langle$ forms, as a result of the ozonization and subsequent oxidative decomposition of the ozonide with hydrogen peroxide, 1-chlorosuccinic acid. The latter splits off HCl under the conditions of treatment of the ozonide, and forms fumaric acid. The formation of fumaric acid, which has a trans structure, gives us reason to conclude that in the original polymer, groups of the chief unit are distributed in such a way as to have a trans structure, as in gutta-percha. It is possible that the properties of the polymer of 1,2,3-trichlorobutadiene-1,3, which are like those of gutta-percha, are related to this trans structure. We cannot, however, consider this as demonstrated, as it is possible that during the splitting off of HCl from chlorosuccinic acid, maleic acid is first formed. Under the action of HCl, the latter can isomerize to give fumaric acid.

EXPERIMENTAL

Various preliminary data on the polymerization of 2,3-dichlorobutadiene-1,3 and 1,2,3-trichlorobutadiene-1,3 are given in the work of Carothers.

For a more detailed investigation of the conditions of polymerization of 2,3-dichlorobutadiene-1,3 and the properties of the polymer formed, polymerization experiments were carried out with the pure compound under various conditions: with the use of regulators at different temperatures, in CCl_4 solution without a regulator, and in the form of an emulsion at room temperature. The experiments carried out showed that the polymerization of 2,3-dichlorobutadiene-1,3 in pure form and with regulators gave a hard, inelastic polymer, insoluble in the usual organic solvents, and stable to various chemical reagents, such as, for example, acids and alkalis. When 2,3-dichlorobutadiene-1,3 was polymerized in CCl_4 solution, the polymer formed was friable, and had neither elasticity nor plasticity. The same sort of product was obtained by polymerization in an emulsion.

In order to show the structure of the polymer of 2,3-dichlorobutadiene-1,3, it was ozonized. In view of the fact that the polymer was insoluble, and hardly swelled in chloroform, its ozonization was very difficult, and in fact it reacted with ozone very slowly. For ozonation, very small amounts required a lengthy period of treatment. For purposes of ozonation, 4.5 g of the polymer was used. This was freed of volatile substances by lengthy extraction in a Soxhlet extractor with ethyl ether.* Samples were cut up into fine pieces and distributed through a 15 to 20 fold excess of chloroform. The ozonation was continued for 48 hours and was ended when a test of the solution showed no decolorization of a solution of bromine in chloroform and gave no precipitate with alcohol. The solvent was driven off in vacuum until the residue was of constant weight. 4.1 g of ozonide was obtained. The latter was decomposed by heating gently with water for an hour. In this way, all the ozonide went into solution, from which the following substances were isolated.

*Which was then driven off until the weight remained constant.

1) Formaldehyde, in the form of a precipitate with dimedon, with m.p. 186°, total 0.52 g. A mixed test of the condensation product with the product of the reaction of dimedon and pure formaldehyde gave no depression of the melting point.

2) 0.27 g of formic acid (determined by the calomel formed during the reaction with corrosive sublimate).

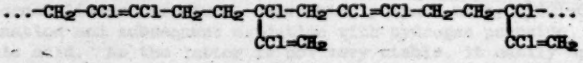
3) 0.38 g of hydrochloric acid.

4) 1.21 g of succinic acid with m.p. 179.5-180°. A mixed test with pure succinic acid melted at 180°. The acid number was 950.2 and 948.3 (computed 951 (Table).

Products of decomposition of ozonide	Obtained by ozonation		Computed for normal structure of polymer
	g	(in % of carbon skeletone of ozonide)	
1. Formaldehyde	0.52	18.07	0
2. Formic acid	0.27	6.10	0
3. Hydrochloric acid ..	0.38	-	1.7
4. Succinic acid	1.21	42.75	2.83

A comparison of the results obtained with those computed theoretically for an ozonide of normal structure of the polymer of 2,3-dichlorobutadiene-1,3, in which the units are linked 1,4-1,4 or 1,4-4,1 shows a considerable deficiency of hydrochloric and succinic acids. The deficiency of the first may be explained by its volatilizing during the ozonation. The deficiency of the succinic acid is more difficult to explain, as under the conditions, with careful treatment, it could not have been lost. In addition, the ozonide reacted very smoothly, and no tar formation was observed. On the other hand, there is the unexplained presence among the cleavage products of the ozonide of considerable amounts of formic acid and formaldehyde. The latter could not be formed by the oxidation of succinic acid under the conditions of ozonation, as its amount is too large for this. Thus, during the ozonolysis of the ω-polymer of chloroprene, the duration of ozonation amounts to 120 to 130 hours, and none the less the amount of formic acid and formaldehyde formed during this time does not exceed 5%. The duration of ozonation of the 2,3-dichlorobutadiene-1,3 is no greater than 48 hours.

We may assume that the original polymer does not have a completely linear structure, and that some of the links are joined in the 1,2 position according to the following scheme:



The absence of high molecular weight acids or of tar resulting from the decomposition of the ozonides of 2,3-dichlorobutadiene may possibly be explained by the fact that the chloroaldehydes or acids formed easily split off HCl, as evidently takes place further along in the case of the decomposition products of the ozonides of 1,2,3-trichlorobutadiene-1,3. The unsaturated acids formed as a result of the splitting off of HCl are further ozonized and are decomposed under the conditions of ozonation, or else there is decomposition of the ozonides to give HCl and CO_2 which were not recovered. This fact, in all probability, explains the low yield of the products of decomposition of the ozonide - 67% of the carbon skeleton.

The scheme for the structure of the polymer of 2,3-dichlorobutadiene

suggested above satisfactorily explains the formation of considerable amounts of formaldehyde and formic acid, which arise, possibly, from the oxidation of the side chains. This also satisfactorily explains the complete insolubility of the polymer of 2,3-dichlorobutadiene. In fact, in the presence of side chains containing double bonds we may expect the very easy formation of spatial structures by the addition of molecules of 2,3-dichlorobutadiene at these side chains.

In order to investigate the structure of the polymer of 1,2,3-trichlorobutadiene, experiments were carried out on its ozonation. For this purpose, 1,2,3-trichlorobutadiene was almost 100% polymerized, and the polymer cut into fine pieces and extracted with ether in a Soxhlet apparatus to remove unpolymerized monomer. After the extraction, the polymer was dried in a vacuum on the water bath to constant weight, and then allowed to swell in chloroform. A 5.3672 g sample of polymer, allowed to swell in 10 times the amount of chloroform, was subjected to the action of ozone for 49 hours, until a test of the solution no longer decolorized a solution of bromine in chloroform. After the solvent was driven off in vacuum, and constant weight attained, 6.15 g of the ozonide was obtained in the form of a viscous oil. The ozonide was then decomposed with 15 ml of a 15% solution of hydrogen peroxide and 30 ml of water by heating on the water bath for 4 hours. A total of 54.54 g of solution was obtained. A test for aldehydes with fuchsine-sulfurous acid gave negative results, and no crystals precipitated with dimedon. Thus, no aldehydes were observed.

0.129 g of carbon dioxide was obtained (determined as $BaCO_3$). The total acidity corresponded to 5.65 g of KOH, and the HCl amounted to 1.42 g (Cl' by Volhard's method), which was equivalent to 2.18 g of KOH. Consequently, the organic acids obtained were equivalent to 3.41 g of KOH. After removal of the water, 3.20 g of organic acids was obtained. The yield of organic acids based on the carbon skeleton of the polymer used was 81.48%. After removal of the volatile and liquid acids, the crystalline acids obtained were recrystallized several times from a mixture of acetone with benzene. The melting point in a sealed capillary was 286-287° (with correction, 297°). This corresponded to the melting point of fumaric acid. A mixed test gave no melting point depression. The acid numbers were 981.26 and 970.64; the acid number computed for fumaric acid was 967.16. The silver salt of a sample of acid weighing 0.1169 g was obtained by neutralizing the acid with a solution of KOH in the presence of an indicator, and adding a saturated solution of $AgNO_3$. The precipitated salt was filtered off in a Schott crucible and dried to constant weight. Computed 65.42% Ag; found 65.69% Ag.

Thus, analysis of the silver salt confirmed the presence of fumaric acid. This pointed to the fact that the polymer of 1,2,3-trichlorobutadiene-1,3 had a normal linear structure. The chief polymer unit, $)CCl-CH_2-CHCl-CCl($, in ozonation and subsequent oxidation with hydrogen peroxide, gives 1-chlorosuccinic acid. As the latter is not very stable, it easily splits off HCl during the treatment, to form fumaric acid.

SUMMARY

The structure of the polymers of 2,3-dichlorobutadiene-1,3 and 1,2,3-trichlorobutadiene-1,3 has been investigated.

1. It was shown that the polymer of 2,3-dichlorobutadiene-1,3 was hard and insoluble in all solvents, and had the character of gutta-percha. The polymer molecule, as shown by the results of ozonolysis (the formation of formic acid and formaldehyde in an amount up to 2% of the carbon skeleton of the polydiene) has a number of side chains, as a result of the addition of the units in the 1,2 position.

2. The polymer of 1,2,3-trichlorobutadiene-1,3 is soluble only during the first stages of polymerization, not beyond the extent of 40%. In this stage, it is rubber-like. At a higher degree of polymerization (above 40%) the polymer becomes hard, has little resemblance, in its physical and mechanical properties, to rubber, and is similar to gutta-percha.

According to the results of ozonolysis, the polymers of 1,2,3-trichlorobutadiene-1,3 have a normal 1,4-1,4 structure (81.5% fumaric acid formed). This structure appears to be linear for the soluble stages. With a higher degree of polymerization (above 40%) branching of the structure takes place, with the formation of spatial, insoluble polymers, which have inner properties like those of gutta-percha.

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DERIVATIVES OF ACETYLENE

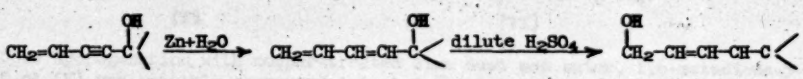
111. THE REARRANGEMENTS OF POLYENE SYSTEMS

VI. THE ALLYL AND TRIENE ISOMERIZATIONS OF 1,6-HEPTADIENE-3-INE-5-OL, 1,3,6-HEPTATRIENE-5-OL, AND 1,3,6-OCTATRIENE-5-OL

I. N. Nazarov and L. B. Fisher

Institute of Organic Chemistry of the Academy of Sciences of the USSR

In preceding communications we have described the rearrangement of an entire series of 1,3-diene alcohols, which were easily obtained by the hydrogenation of the corresponding vinylethinylcarbinols by means of copper-treated zinc dust and water. The isomerization of aliphatic 1,3-diene alcohols is a reversible reaction, which takes place under the influence of dilute solutions of sulfuric acid by displacing the hydroxyl to position 5, with the simultaneous shift of two double bonds of the diene system:



We have now investigated similar isomerization in alcohols containing diene-ine and triene systems.

The action of vinylacetylenylmagnesium bromide on acrolein gave about a 55% yield of 1,6-heptadiene-3-ine-5-ol (I) which upon shaking with 3% sulfuric acid at a temperature of 65-70° for 6 hours was completely isomerized into 1,5-heptadiene-3-ine-7-ol:

(I) (II)

For purposes of comparison, it was of interest to note that according to the data of Jones and McCombie [2] secondary vinylethinylcarbinol (Ia) has no tendency whatever to isomerize to the corresponding primary ethylvinylcarbinol (IIa), even under the influence of 25% sulfuric acid at high temperature. This indicates the considerably lower mobility of the hydroxyl group in the carbinol (Ia) in comparison with that in (I):

(Ia) (IIa)

The hydrogenation of 1,6-heptadiene-3-ine-5-ol (I) with copper-treated zinc dust and water smoothly gives 1,3,6-heptatriene-5-ol (III), which easily isomerizes under the action of 1% sulfuric acid in a solution of aqueous dioxane to give 1,3,5-heptatriene-7-ol (IV) even at room temperature:

$$CH_2=CH-CH=CH-\underset{\underset{OH}{|}}{CH}-CH=CH_2 \longrightarrow CH_2=CH-CH=CH-CH=CH-\underset{\underset{OH}{|}}{CH}-CH_3$$

(III) (IV)

This isomerization also takes place under the action of a 1% aqueous solution of sulfuric acid at room temperature, but is accompanied by considerable tarring, as a result of which it is extremely difficult to separate the carbinol (IV).

The structure of the alcohols described above (I, II, III, and IV) was confirmed by their hydrogenation in the presence of a Pt catalyst. Upon hydrogenation, the secondary alcohols (I and III) absorbed the amounts of hydrogen required by theory (4 and 3 molecules, respectively) and formed ethylbutylcarbinol in both cases; oxidation of the latter with chromic anhydride give ethylbutylketone. Upon hydrogenation, the primary alcohols (II and IV) also absorbed the theoretical amounts of hydrogen (4 and 3 molecules), at the same time forming n-heptyl alcohol, which was identified by its phenylurethane. It gave no depression of the melting point when mixed with a known sample.

The action of vinylacetylenylmagnesium bromide on crotonic aldehyde gave a 75% yield of 1,6-octadiene-3-ine-5-ol (V), which had been previously described by Heilbron and his coworkers. Upon shaking with dilute sulfuric acid, this was easily isomerized to give 1,5-octadiene-3-ine-7-ol (VI) [3]:

$$CH_2=CH-C\equiv C-\underset{\underset{OH}{|}}{CH}-CH=CH-CH_3 \longrightarrow CH_2=CH-C\equiv C-CH=CH-\underset{\underset{OH}{|}}{CH}-CH_3.$$

(V) (VI)

Upon hydrogenation with copper-treated zinc dust and water, 1,6-octadiene-3-ine-5-ol (V) was smoothly converted into 1,3,6-octatriene-5-ol (VII). The latter underwent the allyl isomerization with extraordinary ease to give 1,3,5-octatriene-7-ol (VIII):

$$CH_2=CH-CH=CH-\underset{\underset{OH}{|}}{CH}-CH=CH-CH_3 \longrightarrow CH_2=CH-CH=CH-CH=CH-\underset{\underset{OH}{|}}{CH}-CH_3.$$

(VII) (VIII)

This isomerization took place completely when the carbinol (VII) was shaken with 1% sulfuric acid for one hour even at room temperature.

If 1,3,5-octatriene-7-ol (VIII) is shaken with dilute sulfuric acid for a long time (45 hours) it undergoes the reverse triene isomerization, with the formation of 2,4,6-octatriene-1-ol (IX):

$$CH_2=CH-CH=CH-CH=CH-\underset{\underset{OH}{|}}{CH}-CH_3 \rightleftarrows CH_2OH-CH=CH-CH=CH-CH=CH-CH_3$$

(VIII) (IX)

This rearrangement takes place as a result of the shift of the hydroxyl to position 7, with a simultaneous shift of the triene system [4].

When the secondary alcohols (V and VII) are hydrogenated with Pt catalyst in alcoholic solution, they absorb the theoretical amount of hydrogen (4 and 3 molecules) and form propylbutylcarbinol, whose oxidation with chromic anhydride

gives propylbutylketone. Upon similar hydrogenation of the secondary alcohols (VI and VIII), the theoretical amount of hydrogen is also absorbed (4 and 3 molecules) and they are thus converted into methylhexylcarbinol, whose oxidation with chromic anhydride gives methylhexylketone, identified by a mixed test of its semicarbazone with a known sample.

The primary triene alcohol (IX), upon hydrogenation with Pt catalyst, absorbs the theoretically required 3 molecules of hydrogen and is converted into n-octyl alcohol, characterized by a mixed test of its phenylurethane with a known sample. Upon hydrogenation of the dieneine alcohol (V) by means of copper treated zinc dust and water, there is formed, along with the triene alcohol (VII) a small amount of octatriene (X or XI), which upon hydrogenation with Pt catalyst absorbs 3 molecules of hydrogen and forms n-octane:

$CH_2=CH-CH=CH-CH_2-CH=CH-CH_3$ (X) $CH_2=CH-CH=CH-CH=CH-C_2H_5$ (XI)

The dieneine alcohols (I, II, V, VI) and the secondary triene alcohols (III, VII, VIII) are colorless liquids, which turn yellow and polymerize upon standing. The primary triene alcohols (IV, IX) are colorless crystalline substances, which crystallize in the form of soft, fluffy needles, which also turn yellow upon standing and become hard and brittle.

EXPERIMENTAL

1,6-Heptadiene-3-ine-5-ol (I). An ether solution of vinylacetylenylmagnesium bromide was obtained from 22 g of magnesium, 130 g of ethyl bromide, 60 g of vinylacetylene, and 350 ml of absolute ether. This was stirred continuously in a current of nitrogen and cooled with a mixture of ice and salt (-16°) while a solution of 50 g of acrolein in 50 ml of ether was added over a period of 30 minutes. The reaction mixture was stirred for 4 more hours at the same temperature and allowed to stand overnight. The Grignard complex was decomposed with ice and a saturated solution of ammonium chloride in a current of nitrogen at a temperature of -10°. The product was extracted with ether, dried over sodium sulfate, and distilled under reduced pressure in a current of nitrogen. 52 g of 1,6-heptadiene-3-ine-5-ol (I) was obtained:

B.p. 77-78° at 16 mm; n_D^{20} 1.5040; d_4^{20} 0.9354. MR_D found 34.16; computed 33.11.

4.780 mg substance: 13.645 mg CO_2; 3.283 mg H_2O.
5.810 mg substance: 16.575 mg CO_2; 3.935 mg H_2O.
Found %: C 77.90, 77.85; H 7.68, 7.58.
C_7H_8O. Computed %: C 77.77; H 7.40.

Freshly distilled 1,6-heptadiene-3-ine-5-ol is a completely colorless, transparent, mobile liquid. Upon standing for a month in the presence of pyrogallol, the product was unchanged.

The hydrogenation of 1,6-heptadiene-3-ine-5-ol. Upon hydrogenation, 5.5 g of the carbinol (I) in a solution of 15 ml of alcohol in the presence of Pt catalyst absorbed 4.8 liters of hydrogen (4 mols). Distillation of the product gave 3.5 g of butylethylcarbinol; b.p. 152-154°; n_D^{18} 1.4205. Oxidation of the butylethylcarbinol obtained with chromic anhydride in acetic acid gave 2.6 g of butylethylketone, b.p. 145-146°. The semicarbazone of the ketone melted at 106-107°.

1,5-Heptadiene-3-ine-7-ol (II). A mixture of 6 g of 1,6-heptadiene-3-ine-5-ol (I) (b.p. 77-78° at 16 mm; n_D^{20} 1.5040) and 60 ml of 3% sulfuric acid

was stirred vigorously at a temperature of 65-70° in a stream of nitrogen for 6 hours. After cooling, the upper layer was then removed, and the lower layer salted out with potash, and extracted with ether. The ether solution was washed with water, dried over sodium sulfate, and distilled in a current of nitrogen. 3.3 g of 1,5-heptadiene-3-ine-7-ol (II) was obtained:

B.p. 75-76° at 3 mm; n_D^{20} 1.5520; d_4^{20} 0.9515. MR_D found 36.25; computed 33.11.

5.705 mg substance: 16.290 mg CO_2; 3.875 mg H_2O.
Found %: C 77.92; H 7.60.
C_7H_8O. Computed %: C 77.77; H 7.4.

1,5-Heptadiene-3-ine-7-ol was a completely colorless, transparent liquid, which turned slightly yellow after a day. After 3 days, it was a deep yellow, and a polymer appeared on the walls of the vessel. After 7 days, the product was transformed into a gelatinous polymer.

The hydrogenation of 1,5-heptadiene-3-ine-7-ol. Upon hydrogenation, 1.2 g of the carbinol (II) in a solution of 6 ml of alcohol in the presence of Pt catalyst absorbed 4 molecules of hydrogen (1.08 liters) and 0.85 g of n-heptyl alcohol was obtained; b.p. 78-79° at 15 mm; n_D^{18} 1.4250. The phenylurethane of this n-heptyl alcohol melted at 59-60°, and gave no melting point depression with a known sample.

1,3,6-Heptatriene-5-ol (III). A mixture of 43 g of 1,6-heptadiene-3-ine-5-ol (I) (b.p. 77-78° at 16 mm; n_D^{20} 1.5040), 75 ml of ether, 21 g of copper-treated zinc dust, and 10 ml of water was stirred for 12 hours at 30 to 32°. Then 21 g more of copper-treated zinc dust was added along with 10 ml of water, and the stirring was continued for 12 hours at room temperature and 12 hours at 30-32°. In all, 5 portions of zinc dust and water were added in this fashion. The experiment took 11 days, and the stirring was continued for 123 hours. The usual treatment gave 30 g of 1,3,6-heptatriene-5-ol (III):

B.p. 68-70° at 16 mm; n_D^{20} 1.4995; d_4^{20} 0.8959. MR_D found 36.14; computed 34.64.

4.850 mg substance: 13.485 mg CO_2; 3.975 mg H_2O.
6.385 mg substance: 17.690 mg CO_2; 6.165 mg H_2O.
Found %: C 75.88, 75.61; H 9.17, 9.05.
$C_7H_{10}O$. Computed %: C 76.36; H 9.09.

1,3,6-Heptatriene-5-ol was a colorless, transparent liquid, which after standing for 10 hours was converted into a light yellow, gelatinous polymer. Upon hydrogenation, 2 g of 1,3,6-heptatriene-5-ol in a solution of 8 ml of alcohol absorbed 3 molecules of hydrogen (1.37 liters) and gave 1.2 g of ethylbutylcarbinol, with b.p. 150-152°, n_D^{20} 1.4230.

1,3,5-Heptatriene-7-ol (IV). A solution of 9 g of 1,3,6-heptatriene-5-ol (III) (b.p. 68-70° at 16 mm; n_D^{20} 1.4995) in 75 ml of 60% aqueous dioxane, containing 1% sulfuric acid, was shaken for 3 hours in an atmosphere of nitrogen at room temperature (20°). Then 50 ml of ether was added to the solution and the product was salted out with potash. After removal of the ether and dioxane by distillation in vacuum, the product began to crystallize. 3.6 g of 1,3,5-heptatriene-7-ol (IV) was obtained. B.p. 65-68° at 3 mm. After two recrystallizations from petroleum ether (40-70°), the 1,3,5-heptatriene-7-ol was in the form of white, soft, fluffy needles with m.p. 79-80°. Upon standing, the product turned yellow and became friable.

6.300 mg substance: 17.655 mg CO_2; 5.175 mg H_2O.
Found %: C 76.48; H 9.19.
$C_7H_{10}O$. Computed %: C 76.36; H 9.09.

The hydrogenation of 1,3,5-heptatriene-7-ol. Upon hydrogenation, 1.4 g of carbinol (IV) in a solution of 8 ml of alcohol absorbed 3 molecules of hydrogen (0.91 liter) and gave 1 g of n-heptyl alcohol with b.p. 78° at 15 mm. Its phenylurethane melted at 59-60°, and gave no depression of the melting point with a known sample.

1,6-Octadiene-3-ine-5-ol (V). An ether solution of vinylacetylenylmagnesium bromide was obtained from 20 g of magnesium, 130 g of ethyl bromide, and 60 g of vinylacetylene. To this there was added, with continuous stirring in a current of nitrogen, and with cooling (-15°) a solution of 52 g of crotonic aldehyde in 50 ml of ether. The reaction mixture was stirred 3 more hours at the same temperature and allowed to stand over night. The Grignard complex was disintegrated with ice and a 10% solution of hydrochloric acid, with stirring in a current of nitrogen and cooling to -10°. The product was extracted with ether, dried, and distilled at low pressure in a current of nitrogen. 68 g of the previously described [3] 1,6-octadiene-3-ine-5-ol (V) was obtained; b.p. 67-68° at 3 mm; n_D^{20} 1.5070.

1,3,6-Octatriene-5-ol, (VII). A mixture of 184 g of 1,6-octadiene-3-ine-5-ol (V) (b.p. 67-68° at 3 mm; n_D^{20} 1.5070), 400 ml of ether, 52 g of copper-treated zinc dust, and 30 ml of water were stirred for 15 hours at room temperature and 15 hours at 35 to 40°. In all, there was added in this way 5 portions of zinc dust and water. The stirring was continued for 140 hours. The experiment was continued for 13 days. After the usual treatment, and a thrice-repeated fractional distillation of the product at low pressure in a stream of nitrogen, 6 g of the octatriene (X or XI) was obtained, b.p. 65-67° at 45 mm, and 140 g of the octatriene-5-ol (VII);

B.p. 81-82° at 10 mm; n_D^{20} 1.5030; d_4^{20} 0.8913. MR_D found 41.17. Computed 39.67.

5.760 mg substance: 16.332 mg CO_2; 4.937 mg H_2O.
6.440 mg substance: 18.327 mg CO_2; 5.595 mg H_2O.
Found %: C 77.38, 77.66; H 9.59, 9.72.
$C_8H_{12}O$. Computed %: C 77.41; H 9.67.

1,3,6-Octatriene-5-ol is a completely colorless, transparent, mobile liquid, which does not change upon storage over a period of one year.

The hydrogenation of 1,3,6-octatriene-5-ol. A solution of 2.05 g of the triene alcohol (VII) in 6 ml of alcohol was hydrogenated in the presence of Pt catalyst. 1210 ml of hydrogen (3 mols) were absorbed, and 1.5 g of butylpropylcarbinol was obtained. B.p. 66-67° at 8 mm; n_D^{20} 1.4250; d_4^{20} 0.8173; MR_D found 40.72; computed 40.67.

Upon oxidation with chromic anhydride in acetic acid, 4.2 g of butylpropylcarbinol gave 2.75 g of butylpropylketone, b.p. 46-47° at 8 mm and 162-163° at atmospheric pressure; n_D^{20} 1.4140; d_4^{20} 0.8186; MR_D found 39.12; computed 39.15. The semicarbazone of propylbutylketone melted, in accordance with the data in the literature, at 95°.

Investigation of the octatriene (X or XI). The hydrocarbon obtained was a colorless mobile liquid with the following characteristics:

B.p. 65-67° at 45 mm: n_D^{20} 1.5300; d_4^{20} 0.7815; MR_D found 42.7; computed 37.7.

4.010 mg substance: 12.992 mg CO_2; 3.930 mg H_2O.
6.747 mg substance: 21.877 mg CO_2; 6.620 mg H_2O.
Found %: C 88.62, 88.49; H 10.99, 10.98.
C_8H_{12}. Computed %: C 88.88; H 11.11.

Upon cooling with ice water, the product crystallized in colorless crystals,

which readily deliquesced in the air. A month after the compound had been prepared, it had polymerized into a yellow, spongy polymer.

Upon hydrogenation with Pt catalyst, 4 g of the octatriene in a solution of 10 ml of glacial acetic acid absorbed 2.7 liters of hydrogen (3 mols) and gave 3.1 g of n-octane. B.p. 124-125°; n_D^{18} 1.3982; d_4^{20} 0.7028. Judging by the high exaltation of the molecular refraction (4.4 units) and the rapid polymerization, the hydrocarbon obtained must be regarded as conjugated 1,3,5-octatriene (XI).

1,3,5-Octatriene-7-ol (VIII). A mixture of 35 g of 1,3,6-octatriene-5-ol (VII) (b.p. 81-82° at 10 mm; n_D^{20} 1.5030) and 105 ml of 1% sulfuric acid were shaken at room temperature for 1 hour. After the usual treatment, and a threefold vacuum distillation, 23 g of 1,3,5-octatriene-7-ol (VIII) was obtained in the form of a colorless, transparent, mobile liquid with the following constants:

B.p. 89-90° at 9 mm; n_D^{20} 1.5425; d_4^{20} 0.9009. MR_D found 43.42; computed 39.27.

6.420 mg substance: 18.217 mg CO_2; 5.510 mg H_2O.
5.680 mg substance: 16.100 mg CO_2; 4.820 mg H_2O.
Found %: C 77.43; 77.36; H 9.60, 9.50.
$C_8H_{12}O$. Computed %: C 77.41; H 9.67.

In addition to the 1,3,5-octatriene-7-ol, there was obtained in this experiment 5 g of higher-boiling products (b.p. 90-130° at 9 mm; n_D^{20} 1.5335), and 3 g of substance remained in the distillation flask in the form of a very thick oil. Upon standing for 1 year, 1,3,5-octatriene-7-ol became slightly more viscous, but remained as colorless and transparent as before.

The hydrogenation of 1,3,5-octatriene-7-ol. 5 g of the triene alcohol (VIII) in a solution of 15 ml of alcohol in the presence of Pt catalyst absorbed 2.9 liters of hydrogen (3 mols) and gave 4.4 g of methylhexylcarbinol; b.p. 72-73° at 9 mm; n_D^{20} 1.4260; d_4^{20} 0.8180; MR_D found 40.69; computed 40.67.

Upon oxidation with chromic anhydride in acetic acid, 4.4 g of the methylhexylcarbinol gave 3.5 g of methylhexylketone; b.p. 49-50° at 7 mm and 170-172° at atmospheric pressure; n_D^{20} 1.4152; d_4^{20} 0.8171; MR_D found 39.23; computed 39.15.

The semicarbazone of methylhexylketone melted at 122-123° and gave no depression of the melting point with a known sample.

2,4,6-Octatriene-1-ol (IX). A mixture of 30 g of 1,3,5-octatriene-7-ol (VIII) (b.p. 89-90° at 9 mm; n_D^{20} 1.5425), and 90 ml of 3% sulfuric acid was shaken in an atmosphere of nitrogen at room temperature for 45 hours, and after the usual treatment of the product, was distilled at low pressure in a current of nitrogen.

First fraction: b.p. 83-85° at 6 mm; n_D^{20} 1.5424 – 13 g,
Second fraction: b.p. 83-105° at 3 mm; – 2.5 g,
Third fraction: b.p. 105-125° at 3 mm; n_D^{20} 1.5305 – 2 g.
Residue in flask about 11 g of viscous oil.

The first fraction was the original 1,3,5-octatriene-7-ol. The second fraction began to crystallize in the receiver, and from it was isolated 2 g of 2,4,6-octatriene-1-ol (IX), which after recrystallization from petroleum ether (40 to 70°) was in the form of white needles with a silvery lustre, melted at 99°, and corresponded to the data in the literature [5].

5.560 mg substance: 15.857 mg CO_2; 4.867 mg H_2O.
6.210 mg substance: 17.715 mg CO_2; 5.400 mg H_2O.
Found %: C 77.88, 77.85; H 9.79, 9.73.
$C_8H_{12}O$. Computed %: C 77.41; H 9.67.

Upon storage for 6 months, 2,4,6-octatriene-1-ol turned yellow, but did not lose its silvery lustre.

Exactly the same result was obtained by the isomerization, under the conditions described above, of 1,3,6-octatriene-5-ol (shaking with 3% sulfuric acid for 45 hours at room temperature).

The hydrogenation of 2,4,6-octatriene-1-ol. 0.7 g of the primary triene alcohol (IX) in a solution of 10 ml of alcohol absorbed 400 ml of hydrogen (3 mols) and gave 0.5 g of n-octanol-1, which boiled at 79° at 7 mm; n_D^{18} 1.4315. The phenylurethane of this octanol melted at 73°, and a mixed test with a known sample gave no depression of the melting point.

SUMMARY

The action of vinylacetylenylmagnesium bromide on acrolein gave a 55% yield of dieneine alcohol (I), which upon shaking with 3% sulfuric acid at a temperature of 69-70° was completely isomerized into the conjugated dieneine alcohol (II). The dieneine alcohol (I) is smoothly hydrogenated by means of copper-treated zinc dust and water to give the triene alcohol (III), which is easily isomerized into the conjugated triene alcohol (IV) under the influence of 1% sulfuric acid even at room temperature.

Similarly, the dienine alcohol (V), formed with a yield of 75% by the action of vinylacetylenyl magnesium bromide on crotonic aldehyde, is smoothly hydrogenated by means of copper-treated zinc dust and water to give the triene alcohol (VII), and the latter is isomerized with extraordinary ease into the conjugated triene alcohol (VIII) under the action of 1% sulfuric acid at room temperature.

The secondary triene alcohol (VIII), upon shaking with 1% sulfuric acid at room temperature, undergoes a slow reversible isomerization into the primary triene alcohol (IX) by a shift of the hydroxyl to position 7, with a simultaneous shift of the three double bonds of the conjugated triene system.

Upon hydrogenation of the dieneine alcohol (V) with zinc dust and water, there was obtained, in addition to the triene alcohol (VII) a small yield (about 3%) of octatriene (X or XI), formed by the reduction of the hydroxyl group.

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[2] Jones and McCombie, J.Chem.Soc., 261 (1943).

[3] Heilbron, Jones, and McCombie, J.Chem.Soc., 140 (1944).

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DERIVATIVES OF ACETYLENE

112. THE REARRANGEMENTS OF POLYENE SYSTEMS

VII. THE SYNTHESIS AND ISOMERIZATION OF STYRYLVINYLETHINYLCARBINOL, STYRYLBUTADIENYLCARBINOL, FURYLVINYLETHINYLCARBINOL AND FURYLBUTADIENYLCARBINOL

L. N. Nazarov and L. B. Fisher

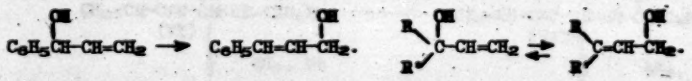
Institute of Organic Chemistry of the Academy of Sciences of the USSR

As has been shown in one of our preceding communications [1], phenylbutadienylcarbinol is easily and irreversibly isomerized under the influence of dilute solutions of sulfuric acid into the corresponding primary diene alcohol (1-phenyl-1,3-pentadiene-5-ol):

In contradistinction to these alcohols, the aliphatic diene carbinols undergo reversible isomerization, the primary alcohols being isomerized with greater speed than the secondary and tertiary butadienylcarbinols isomeric with them [2]:

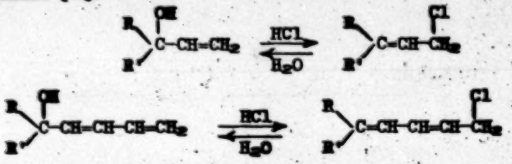
R and R' equal alkyl or hydrogen.

The same rules hold true also during the isomerization of the substituted allyl alcohols. Phenylvinylcarbinol, as is known, is easily and irreversibly isomerized under the influence of dilute solutions of sulfuric acid into cinnamic alcohol [3], while allyl alcohols with aliphatic radicals are isomerized more slowly and always reversibly:



In this process, the primary γ,γ-dialkylallyl alcohols isomerize with much greater speed than the tertiary dialkylvinylcarbinols [4] which are its isomers. The tendency of the hydroxyl to assume a tertiary position in the allyl and diene alcohols (in contradistinction to the atom of chlorine, which tends to occupy the primary position) is especially clearly illustrated by the interchange reactions of these alcohols with hydrogen chloride, during which the primary chlorides are

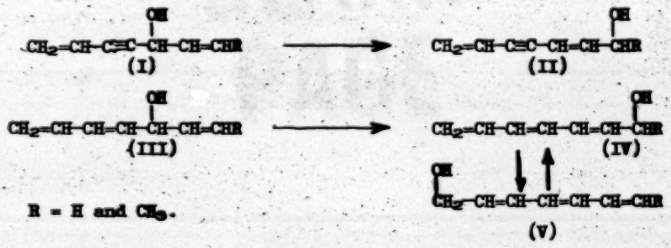
chiefly formed, while the hydrolysis of these clorides once more gives the tertiary alcohols [5]:



The allyl, diene, and polyene isomerizations take place with especial ease in the case where the hydroxyl group is attached to a carbon related to two unsaturated systems. Thus, Heilbron, Jones, and their associates [6] have recently described the rearrangement of a large number of alcohols which contain in their allyl or polyene systems acetylene or vinylacetylene groups as well:

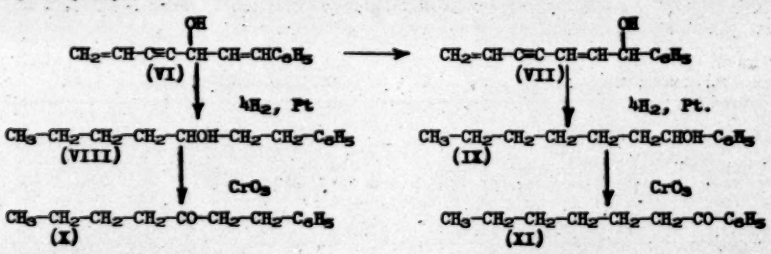
All these rearrangements take place with extraordinary ease, and irreversibly, a result which is explained by the fact that isomerization produces a stable conjugated system.

In a previous communication we have described the rearrangements of alcohols containing vinyl and vinylacetylenyl at the same time, as well as vinyl and diene groups, as in the following examples [7]:



R = H and CH_3.

It was of interest to consider the influence of aromatic radicals on the course of these rearrangements. With this purpose in mind, we used the action of vinylacetylenylmagnesium bromide on cinnamic aldehyde to synthesize styrylvinylethinylcarbinol (VI) in 84% yield. Under the action of 3% sulfuric acid in aqueous dioxane, this was irreversibly isomerized into 7-phenyl-1,5-heptadiene-3-ine-7-ol (VII).



In this connection we must note that styrylethinylcarbinol (VIa), according to the data of Jones and McCombie [8] showed no tendency whatever to isomerize to give the phenylethinylvinylcarbinol (VIIa) which corresponds to it:

(VIa) (VIIa)

The simplest analogs of alcohols (VI and VIa), which contain hydrogen atoms in place of the phenyls, behave in the same way with regard to isomerization.

Thus, the allyl alcohols which contain vinylacetylene radicals are distinguished by the much greater mobility of their hydroxyl, and by their greater tendency to isomerize in comparison with the corresponding alcohols which contain acetylene radicals.

Upon hydrogenation of the dieneine alcohols (VI and VIa) in the presence of Pt catalyst, 4 molecules of hydrogen are absorbed and the corresponding saturated alcohols (VIII and IX) are obtained. These were oxidized with chromic oxide to give the corresponding ketones (X and XI). The latter were identified by a comparison with synthetic samples obtained by the action of hexylmagnesium bromide on benzaldehyde, followed by oxidation of the alcohol (IX) with chromic anhydride. Both of the samples of phenylhexylketone obtained were the same, and their semicarbazones gave no melting point depression in a mixed test.

The styrylvinylethinylcarbinol (VI) was hyrogenated by means of copper-treated zinc dust to give 7-phenyl-1,3,6-heptatriene-5-ol (XII), which, under the influence of 1% sulfuric acid in a solution of aqueous dioxane, was also irreversibly isomerized into 7-phenyl-1,3,5-heptatriene-7-ol, (XIII):

(XII) (XIII)

The triene alcohols (XII and XIII), upon hydrogenation with Pt catalyst, absorbed 3 molecules of hydrogen and were converted into the corresponding saturated alcohols (VIII and IX), which in this case too were oxidized with chromic anhydride into the ketones corresponding to them (X and XI).

Under the influence of 1% sulfuric acid in aqueous dioxane, 7-phenyl-1,3,5-heptatriene-7-ol (XIII) in its turn underwent isomerization to give 7-phenyl-2,4,6-heptatriene-1-ol (XIV), which in the last analysis means a rearrangement of the hydroxyl in position 7, with a simultaneous shift of the three double bonds of the conjugated triene system:

$$CH_2OH-CH=CH-CH=CH-CH=CH-C_6H_5.$$

(XIV)

Although the primary triene alcohol (XIV) was not successfully obtained in pure form, its formation was shown beyond the possibility of doubt by hydrogenation and the isolation of 7-phenylheptane-1-ol (XV), the latter being then oxidized to give 7-phenylheptane-1-carboxylic acid (XVI):

$$C_6H_5-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2OH \longrightarrow C_6H_5-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-COOH.$$

(XV) (XVI)

The rearrangements described above, VI → VII and XII → XIII, take place with much more difficulty than the rearrangments of the alcohols which correspond to them, I → II and III → IV, and contain methyl radicals in place of the phenyls.

This is without doubt related to the retarding influence of the electronegative phenyl group.

However, despite this, alcohol (XII) is isomerized by way of the allyl rearrangement, into the secondary triene alcohol (XIII), whereas the diene rearrangement of alcohol (XII) into the primary triene alcohol (XIV) either does not take place at all or takes place to only a very slight degree.

The alcohol (III; R = CH_3), as has already been noted in a previous communication, behaves similarly and even more strikingly. This is isomerized (with extraordinary ease) only into the secondary triene alcohol (IV), and does not undergo the diene rearrangement to give the primary triene alcohol (V; R = CH_3) at all. The latter is formed only as the result of a further triene isomerization of the alcohol (IV); (R = CH_3).

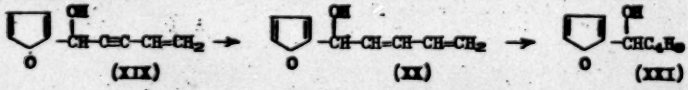
Thus, we have shown a very interesting fact: triene alcohols of the type (III and XII), whose hydroxyl groups are at the same time part of both allyl and pentadiene systems, undergo only the allyl rearrangement, and show no tendency whatever toward the diene isomerization. The triene ion (a), formed by removing the hydroxyl from alcohols (III and XII), is isomerized, therefore, only on the allyl group side into the triene ion (b), which in its turn can slowly isomerize into the triene ion (c). But the direct conversion of ion (a) into ion (c) does not take place:

These facts show that the rearrangement of the allyl group, which is accompanied by the shift of a single double bond, takes place with considerably greater ease than the rival rearrangement of the diene system which is accompanied by the shift of two double bonds. On this basis, we may expect that the resistance of the polyene system to rearrangement will increase along with an increase in the number of conjugated double bonds in the system.

Upon hydrogenation of the styrylvinylethinylcarbinol (VI) by means of copper-treated zinc dust and water, there is obtained along with the triene alcohol (XII) a phenylheptatriene as well, whose structure is given by formulas (XVII or XVIII):

We observed a similar reduction of the hydroxyl group during the hydrogenation of carbinol with zinc dust and water (I; R = CH_3).

We further attempted to show the nature of the above rearrangements by using the corresponding furylcarbinols. The action of vinylacetylenylmagnesium bromide on furfural gave α-furylvinylethinylcarbinol (XIX), which was fairly easily hydrogenated with copper-treated zinc dust and water to give α-furylbutadienylcarbinol (XX):



The furan alcohols (XIX and XX), upon hydrogenation with Pt catalyst, absorbed 3 and 2 molecules of hydrogen respectively, and were converted into

α-furylbutylcarbinol (XXI). All attempts to carry out the isomerization of the furylcarbinols (XIX and XX) gave negative results, because of their extreme instability and their tendency to form tar. The synthesis of α-furylvinylethinylcarbinol (XIX), as well as of styrylvinylethinylcarbinol (VI), must be carried out with good cooling, and in an atmosphere of nitrogen. The distillation of the carbinol must also be carried out in a stream of nitrogen at as low pressure as possible and in small portions (5 or 10 g each). Otherwise the reaction product often decomposes and breaks up during the distillation [8].

EXPERIMENTAL

The synthesis of styrylvinylethinylcarbinol. An ether solution of vinylacetylenylmagnesium bromide was prepared in the usual way from 15 g of magnesium, 100 g of ethyl bromide, 50 g of vinylacetylene, and 300 ml of absolute ether. With continuous stirring and cooling, there was added over a period of 25 minutes, in a current of nitrogen, a solution of 50 g of cinnamic aldehyde (b.p. 128-130° at 18 mm; n_D^{20} 1.6195) in 50 ml of ether. The reaction mixture was stirred for 3 hours at the same temperature and then allowed to stand overnight. The Grignard complex was decomposed in a current of nitrogen with ice and a saturated solution of ammonium chloride at a temperature of -12°, and the product was extracted with ether. The ether solution was dried over sodium sulfate, the ether removed at low pressure in a current of nitrogen, and the product was distilled in small portions of 8 or 10 g, also at low pressure in a current of nitrogen. 58 g of styrylvinylethinylcarbinol (VI) was obtained:

B.p. 140-141° at 2 mm; n_D^{20} 1.6005; d_4^{20} 1.0394. MR_D found 60.6; computed 57.2.

5.600 mg substance: 17.360 mg CO_2; 3.295 mg H_2O.
6.140 mg substance: 18.987 mg CO_2; 3.733 mg H_2O.
Found %: C 84.60, 84.39; H 6.58, 6.58.
$C_{13}H_{12}O$. Computed %: C 84.78; H 6.52.

Freshly distilled styrylvinylethinylcarbinol is a light yellow, transparent liquid. Upon storage for 6 months it is converted into a brown, viscous liquid.

During the synthesis of styrylvinylethinylcarbinol, the conditions indicated above must be strictly observed. When they are altered, the compound decomposes and falls apart during the distillation.

The hydrogenation of styrylvinylethinylcarbinol. 5.2 g of the carbinol (VI) was hydrogenated in 15 ml of alcohol in the presence of Pt catalyst. 4 molecules of hydrogen (2.75 liters) were absorbed, and 4.5 g of 7-phenylheptane-5-ol (VIII) was obtained.

B.p. 136-138° at 7 mm; n_D^{20} 1.5040; d_4^{20} 0.9446, MR_D found 60; computed 60.15.

5.138 mg substance: 15.242 mg CO_2; 4.863 mg H_2O.
5.580 mg substance: 16.582 mg CO_2; 5.272 mg H_2O.
Found %: C 80.96, 81.10; H 10.59, 10.57.
$C_{13}H_{20}O$. Computed %: C 81.25; H 10.41.

Upon oxidation with chromic anhydride in acetic acid, 4.5 g of 7-phenylheptene-5-ol gave 3 g of butyl-β-phenylethylketone (X):

B.p. 125-128° at 7 mm; n_D^{20} 1.4980; d_4^{20} 0.9391. MR_D found 59.2; computed 58.6.

The 2,4-dinitrophenylhydrazone of butyl-β-phenylethylketone melted at 130-132°.

3.620 mg substance: 0.478 ml N_2 (19°, 753 mm).
4.200 mg substance: 0.559 ml N_2 (20°, 753 mm).
Found %: N 15.29, 15.36.
$C_{10}H_{22}N_4O_4$. Computed %: N 15.13.

The isomerization of styrylvinylethinylcarbinol. A solution of 7.3 g of styrylvinylethinylcarbinol (b.p. 140-141° at 2 mm; n_D^{20} 1.6005) and 146 ml of 70% aqueous dioxane containing 3% of sulfuric acid, were heated for 12 hours at 40-45° in a current of nitrogen in the presence of pyrogallol. After cooling, the upper layer was removed, and the aqueous layer was salted out with potash, and extracted with ether. The ether solution was washed with water and dried over sodium sulfate. A distillation of the product at low pressure in a current of nitrogen gave 3 g of 7-phenyl-1,5-heptadiene-3-ine-7-ol (VII):

B.p. 139-141° at 2 mm; n_D^{20} 1.6002; d_4^{20} 1.0396.

5.56 mg substance: 17.35 mg CO_2; 3.29 mg H_2O.
Found %: C 84.65; H 6.60.
$C_{13}H_{12}O$. Computed %: C 84.78; H 6.52.

3 g of undistillable tar remained in the distillation flask.

The hydrogenation of 7-phenyl-1,5-heptadiene-3-ine-7-ol. 2.35 g of carbinol (VII) in a solution of 10 ml of alcohol were hydrogenated in the presence of Pt catalyst. 1.24 liters of hydrogen (4 mols) were absorbed. 2.1 g of phenylhexylcarbinol (IX) were obtained; b.p. 135°-138° at 7 mm; n_D^{20} 1.5024.

Upon oxidation with chromic anhydride in a solution of acetic acid, 2.1 g of phenylhexylcarbinol gave 1.3 g of phenylhexylketone.

B.p. 129-131° at 7 mm; n_D^{20} 1.5060; d_4^{20} 0.9505 MR_D found 59.3; computed 58.6.

The semicarbazone of this phenylhexylketone melted, in conformity with the data in the literature, at 118-119°, and gave no lowering with the semicarbazone of synthetic phenylhexylketone obtained by the oxidation of phenylhexylcarbinol synthesized from benzaldehyde and hexylmagnesium bromide (cf. below).

3.140 mg substance: 0.465 ml N_2 (23°, 755 mm).
3.880 mg substance: 0.575 ml N_2 (23°, 753 mm).
Found %: N 16.96, 16.93.
$C_{14}H_{21}ON_3$. Computed %: N 17.0.

The 2,4-dinitrophenylhydrazone of the above phenylhexylketone melted at 137-139°, and also gave no depression when mixed with a known sample; a mixed test with the 2,4-dinitrophenylhydrazone of butyl-β-phenylethylketone (m.p. 130-132°) gave m.p. 105-118°, i.e., there was considerable depression of the melting point.

The synthesis of phenylhexylcarbinol. A Grignard reagent was prepared from 3 g of magnesium and 20 g of hexyl bromide, and 14 g of benzaldehyde was added over a period of 30 minutes at a temperature of -10°. The reaction mixture was then stirred for two hours and allowed to stand overnight. The next day the reaction mixture was stirred for 5 hours at the boiling point of the ether and the product was then cooled and decomposed with water (10 ml) and then with 10% hydrochloric acid (28 ml). After the usual treatment, 5 g of unreacted benzaldehyde and 10 g of phenylhexylcarbinol were obtained:

B.p. 135-137° at 7 mm; n_D^{20} 1.5020; d_4^{20} 0.9386. MR_D found 60.38; computed 60.15.

The oxidation of phenylhexylcarbinol. To a solution of 8 g of phenylhexylcarbinol in 25 ml of glacial acetic acid there was added a solution of 7.5 g

of chromic anhydride in 25 ml of glacial acetic acid and 4 ml of water. The temperature of the reaction was maintained during the oxidation at 10-15°, and the liquid was then allowed to stand for 2 hours. The acetic acid was neutralized with a 20% solution of caustic soda, the product extracted with ether, dried, and distilled. 5.6 g of phenylhexylketone was obtained:

B.p. 138-139° at 10 mm; n_D^{20} 1.5065; d_4^{20} 0.9511. MR_D found 59.5; computed 58.6.

The semicarbazone of phenylhexylketone melted at 118-119°; the 2,4-dinitrophenylhydrazone melted at 137-139°.

The hydrogenation of styrylvinylethinylcarbinol with copper-treated zinc dust and water. A mixture of 50 g of styrylvinylethinylcarbinol (b.p. 140-141° at 2 mm; n_D^{20} 1.6005), 125 ml of ether, 24 g of copper-treated zinc dust, and 10 ml of water was stirred for 15 hours at room temperature and 15 hours at 28-30°. Then an additional 24 g of copper-treated zinc dust and 10 ml of water was added, and the stirring continued another 15 hours at room temperature and 15 hours at 28-30°. In all, 5 portions of zinc dust and water were thus added. The stirring was continued for 164 hours, and the experiment lasted 15 days. The usual treatment of the product, and three distillations in a current of nitrogen at low pressure gave:

First fraction: b.p. 120-130° at 2 mm; n_D^{20} 1.6160 – 16 g,

Second fraction: b.p. 130-131° at 2 mm; n_D^{20} 1.5970 – 18 g.

The second fraction was pure 7-phenyl-1,3,6-heptatriene-5-ol (XII);

B.p. 130-131° at 2 mm; n_D^{20} 1.5970; d_4^{20} 1.0210. MR_D found 62.07; computed 59.7.

4.827 mg substance: 14.897 mg CO_2; 3.235 mg H_2O.
5.740 mg substance: 17.675 mg CO_2; 3.774 mg H_2O.
Found %: C 84.12, 84.03; H 7.50, 7.36.
$C_{13}H_{14}O$. Computed %: C 83.87; H 7.52.

The first fraction was also 7-phenyl-1,3,6-heptatriene-5-ol (XII) with phenylheptatriene (XVII or XVIII) as impurity. This was formed by the reduction of the hydroxyl group in the carbinol, (XII).

If during the hydrogenation of styrylvinylethinylcarbinol with copper-treated zinc dust and water the temperature is maintained at 35-40°, as in the hydrogenation of crotylvinylethinylcarbinol (cf. preceding communication), a mixture is obtained which consists chiefly of phenylheptatriene, with a small amount of 7-phenyl-1,3,6-heptatriene-5-ol, boiling at 105-125° at 2 mm. The product obtained in this way crystallizes during the distillation, but during several attempts to separate crystals by recrystallization, the product deliquesced in the air. After numerous distillations, it was possible to isolate phenylheptatriene (XVII or XVIII):

B.p. 108-110° at 2 mm; n_D^{20} 1.6330.

8.970 mg substance: 29.540 mg CO_2; 6.627 mg H_2O.
Found %: C 89.87; H 8.26.
$C_{13}H_{14}$. Computed %: C 91.76; H 8.23.

The hydrogenation of 7-phenyl-1,3,6-heptatriene-5-ol. 2.35 g of the carbinol (XII) in a solution of 12 ml of alcohol was hydrogenated in the presence of Pt catalyst. 0.96 liter of hydrogen (3 mols) was absorbed, and 1.9 g of the 7-phenylheptane-5-ol described previously was obtained.

B.p. 135-137° at 7 mm; n_D^{20} 1.5042; d_4^{20} 0.9452.

Upon oxidation of 1.9 g of 7-phenylheptane-5-ol with chromic anhydride, 1.3 g of butyl-β-phenylethylketone was obtained; b.p. 125-128° at 7 mm; n_D^{20} 1.4985; d_4^{20} 0.9391. The 2,4-dinitrophenylhydrazone of butyl-β-phenylethylketone melted at 130-132°, and a mixed test using the sample described above gave no depression.

The hydrogenation of phenylheptatriene. 3 g of phenylheptatriene (b.p. 108°-110° at 2 mm; n_D^{20} 1.6330) in a solution of 10 ml of glacial acetic acid was hydrogenated in the presence of Pt catalyst. 1.11 liters of hydrogen were absorbed (3 mols). 2.25 g of 1-phenylheptane was obtained:

B.p. 99-100° at 6 mm; n_D^{20} 1.4870; d_4^{20} 0.8565.

6.140 mg substance: 19.889 mg CO_2; 6.330 mg H_2O.
5.795 mg substance: 18.790 mg CO_2; 5.960 mg H_2O.
Found %: C 88.40, 88.49; H 11.54, 11.50.
$C_8H_{12}O$. Computed %: C 88.63; H 11.36.

The isomerization of 7-phenyl-1,3,6-heptatriene-5-ol. A) A solution of 4 g of 7-phenyl-1,3,6-heptatriene-5-ol (b.p. 130-132° at 2 mm; n_D^{20} 1.5970) in 80 ml of 70% aqueous dioxane containing 1% sulfuric acid was heated for 1 hour at 40-45° in a current of nitrogen in the presence of pyrogallol. After cooling, the product was extracted with ether, dried over sodium sulfate, and distilled at low pressure in a current of nitrogen:

First fraction: 130-142° at 2 mm; n_D^{20} 1.6062 – 1.2 g.
Second fraction: b.p. 142-145° at 2 mm: 1 g.

The first fraction was a mixture of the original alcohol and the isomeric phenylheptatrieneol (XIII) The second fraction, which consisted of 7-phenyl-1,3,5-heptatriene-7-ol (XIII), crystallized, but it was impossible to purify the product by recrystallization because of its oxidation in the air. After the second fraction was distilled for a second time at low pressure, the 7-phenyl-1,3,5-heptatriene-7-ol (XIII) obtained was analyzed.

6.888 mg substance: 21.109 mg CO_2; 4.370 mg H_2O.
6.350 mg substance: 19.452 mg CO_2; 4.087 mg H_2O.
Found %: C 83.63, 83.60; H 7.10, 7.20.
$C_{13}H_{14}O$. Computed %: C 83.87; H 7.52.

Hydrogenation of the products of isomerization obtained from two such experiments as are described above gave a mixture consisting of 7-phenyl-heptane-5-ol (VIII), phenylhexylcarbinol (IX), and a small quantity of 7-phenylheptane-1-ol (XV).

Upon oxidation, this mixture of alcohols gave a mixture of ketones, which consisted of butyl-β-phenylethylketone and phenylhexylketone, identified by means of their 2,4-dinitrophenylhydrazones. In addition to these ketones, the oxidation gave a small amount of 7-phenylheptane-1-carboxylic acid, whose silver salt was analyzed with the following results:

0.1338 g substance: 0.0456 g Ag.
0.1478 g substance: 0.0510 g Ag.
Found %: Ag 34.13, 34.55.
$C_{13}H_{17}O_2Ag$. Computed %: Ag 34.45.

B) A solution of 4.5 g of 7-phenyl-1,3,6-heptatriene-5-ol in 90 ml of 70% aqueous dioxane containing 1% of sulfuric acid was heated at 40-45° for 2 hours and then treated as in the preceding experiment. After the ether and dioxane had been removed by distilling in vacuum, the products of isomerization were dissolved in ethyl alcohol and hydrogenated in the presence of Pt catalyst. Distillation

of the products of hydrogenation from three such experiments gave the following fractions:

Fraction I: b.p. 128-130° at 4 mm; n_D^{20} 1.5030 - 4 g,

Fraction II: b.p. 130-135° at 4 mm; n_D^{20} 1.5102 - 3 g,

Fraction III: B.p. 135° at 4 mm; n_D^{20} 1.5145 - 2 g.

The first fraction was phenylhexylcarbinol (IX), which upon oxidation with chromic anhydride gave phenylhexylketone, whose 2,4-dinitrophenylhydrazone melted at 137-139° and gave no melting point depression when mixed with a synthetic sample.

The second fraction consisted of a mixture of phenylhexylcarbinol and 7-phenylheptane-1-ol. The third fraction consisted of 7-phenylheptane-1-ol (XV):

B.p. 135° at 4 mm: n_D^{20} 1.5145; d_4^{20} 0.9619. MR_D found 60.2; computed 60.15.

6.700 mg substance: 19.877 mg CO_2; 5.990 mg H_2O.
4.640 mg substance: 13.722 mg CO_2; 4.146 mg H_2O.
Found %: C 80.96, 81.00; H 10.00, 10.00.
$C_{13}H_{20}O$. Computed %: C 81.25; H 10.41.

Oxidation of the 7-phenylheptane-1-ol with chromic anhydride in acetic acid gave 7-phenylheptane-1-carboxylic acid, which was characterized by means of its silver salt.

0.1272 g substance: 0.0444 g Ag.
0.0952 g substance: 0.0333 g Ag.
Found %: Ag 34.98, 34.95.
$C_{13}H_{17}O_2Ag$. Computed %: Ag 34.45.

The synthesis of α-furylvinylethinylcarbinol. Vinylacetylenylmagnesium bromide was obtained from 30 g of magnesium, 200 g of ethyl bromide, and 100 g of vinylacetylene. To this was added, drop by drop, a solution of 90 g of freshly distilled furfural in 90 ml of absolute ether at a temperature of -19°. The product was further treated as in the synthesis of styrylvinylethinylcarbinol (VI). 82 g of α-furylvinylethinylcarbinol (XIX) were obtained:

B.p. 84-85° at 2 mm; n_D^{20} 1.5380; d_4^{20} 1.0913; MR_D found 43.08; computed 41.33.

4.565 mg substance: 12.177 mg CO_2; 2.080 mg H_2O.
4.000 mg substance: 10.670 mg CO_2; 1.876 mg H_2O.
Found %: C 72.79; 72.79; H 5.10, 5.25.
$C_9H_8O_2$. Computed %: C 72.97; H 5.4.

The freshly distilled furylvinylethinylcarbinol was a light yellow liquid. Upon standing for 1 month it turned into a light brown liquid, and after 2 months, into a solid polymer.

The hydrogenation of α-furylvinylethinylcarbinol. A solution of 3.5 g of the carbinol in 15 ml of alcohol was hydrogenated in the presence of Pt catalyst. After 3 molecules of hydrogen (1788 ml) had been absorbed, the hydrogenation was suspended (further hydrogenation would attack the furan ring). A fractional distillation gave 2.9 g of α-furylbutylcarbinol (XXI):

B.p. 68-69° at 2 mm; n_D^{20} 1.4708; d_4^{20} 0.9908. MR_D found 43.4; computed 43.8.

Furylbutylcarbinol was also obtained by a Grignard synthesis from butyl chloride and furfural. The alcohol obtained had the following constants:

B.p. 68-69° at 2 mm; n_D^{20} 1.4710; d_4^{20} 0.9898.

The hydrogenation of α-furylvinylethinylcarbinol with copper-treated zinc dust and water. A mixture of 100 g of α-furylvinylethinylcarbinol (b.p. 84°-85° at 2 mm; n_D^{20} 1.5380), 200 ml of ether, 48 g of copper-treated zinc dust, and 20 ml of water was stirred for 15 hours at room temperature and 15 hours at 30-32°. Then an additional 48 g of copper-treated zinc dust and 20 ml of water were added, and the stirring continued for 15 hours at room temperature and 15 hours at 30-32°. In all, 5 portions of copper-treated zinc dust and water were thus added. The experiment took 12 days. The stirring was continued for 145 hours. After treatment, the product was repeatedly fractionated in vacuum:

Fraction I: b.p. 50-55° at 2 mm; n_D^{20} 1.5462; 4 g,

Fraction II: b.p. 55-82° at 2 mm; n_D^{20} 1.5405; 2 g,

Fraction III: b.p. 82-84° at 2 mm; n_D^{20} 1.5360; 68 g.

The third fraction consisted of α-furylbutadienylcarbinol (XX):

B.p. 83-84° at 2 mm; n_D^{20} 1.5360; d_4^{20} 1.0770. MR_D found 43.46; computed 42.86.

6.955 mg substance: 18.317 mg CO_2; 3.944 mg H_2O.
4.820 mg substance: 12.709 mg CO_2; 2.865 mg H_2O.
Found %: 71.88, 71.96; H 6.34, 6.60.
$C_8H_{10}O_2$. Computed %: C 72; H 6.66.

The freshly distilled α-furylbutadienylcarbinol was a fairly mobile liquid with a pale yellow color. Upon standing even in the presence of pyrogallol for 3 months, the carbinol turned into a dark brown viscous liquid.

The hydrogenation of α-furylbutadienylcarbinol. A solution of 2.1 g of the substance in 10 ml of alcohol was hydrogenated in the presence of Pt catalyst. After 0.7 liter of hydrogen (2 mol) had been absorbed, the hydrogenation was discontinued. 1.65 g of α-furylbutylcarbinol was obtained; b.p. 69-70° at 2 mm; n_D^{20} 1.4720.

SUMMARY

The action of vinylacetylenylmagnesium bromide on cinnamic aldehyde gave styrylvinylethinylcarbinol (VI) in 84% yield. Under the action of 3% sulfuric acid in aqueous dioxane, this isomerized into phenyldivinylacetylenylcarbinol (VII). Upon hydrogenation with copper-treated zinc dust and water, styrylvinylethinylcarbinol (VI) was transformed fairly smoothly into styrylbutadienylcarbinol (XII), which under the influence of 1% sulfuric acid in a solution of aqueous dioxane was also isomerized irreversibly into phenylhexatrienylcarbinol (XIII). Under the action of dilute sulfuric acid, the latter underwent further triene isomerization, the hydroxyl shifting from position 7 to form a primary triene alcohol (XIV). The isomerization described above took place with greater difficulty than in the case of the analogous alcohols with methyl radicals.

The action of vinylacetylenylmagnesium bromide on furfural gave α-furylvinylethinylcarbinol (XIX) in 66% yield. By means of copper-treated zinc dust and water this was hydrogenated to give α-furylbutadienylcarbinol (XX). However, all attempts to carry out the isomerization of these carbinols under the action of dilute solutions of sulfuric acid were unsuccessful, as a result of their extreme instability and their tendency to form tar.

Hydrogenation of styrylvinylethinylcarbinol (VI) by means of copper-treated zinc dust and water also gave phenylheptatriene (XVII or XVIII) formed as a result of the reduction of the hydroxyl group in styrylbutadienylcarbinol (XII).

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